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**ELECTRON-DONATING MACROMOLECULES
BASED ON THIO-CYCLIC UNITS**

TAKASHI UEMURA

2002

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Preface

The study presented in this thesis has been carried out under the direction of Professor Yoshiki Chujo at the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University during April, 1997 – March, 2002. This study is concerned with preparations of functional macromolecules with electron-donating dithiafulvene or thioketene dimer unit, and their optical, electrochemical and conducting properties.

The author wishes to express his sincerest gratitude to Professor Yoshiki Chujo for his kind guidance, valuable suggestions and encouragement throughout this work. The author is deeply and heartily grateful to Associate Professor Kensuke Naka for his constant advices and helpful discussions during the course of this work. The author is also indebted to Dr. Yasuhiro Morisaki for his valuable suggestions and discussions. The author would like to thank Dr. Sujata Marathe, Ms. Adriana Gelover-Santiago, and Mr. Shinsuke Inagi for their great contributions to this work and is thankful to all the members of Professor Chujo's group for their active collaborations. The author is much obliged to Ms. Masako Yokoi for her assistance during the author's school life.

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Takashi Uemura

March 2002

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General Introduction

General Introduction

Dithiafulvenes as Organic Conductors

Dithiafulvenes are the molecules containing two sulfur atoms in the fulvene structure and can form 1,3-dithiolium cations by an easy one-electron oxidation. The 1,3-dithiolium ion is an unsaturated five-membered-ring cation in which each sulfur atom contributes a pair of $3p\pi$ electrons and, consequently, would be expected to show aromatic stability.¹ The chemistry of the dithiafulvene and its derivatives has been a subject of intense interest for the last several decades. Many dithiafulvene derivatives are now well-established as building blocks in the widespread fields of materials chemistry.² The prominent features of the dithiafulvene are as follows.

- (i) Dithiafulvene derivatives behave as π -electron donors and form stable charge-transfer complexes and radical ion salts with a wide variety of organic and inorganic acceptor species.
- (ii) Oxidative dimerizations of the dithiafulvenes by both cyclic voltammetry (CV) and chemical method afford dimeric dication.³
- (iii) The oxidation potentials can be finely tuned by the attachment of substituents. Delocalized π -electron systems of the dithiafulvenes show low oxidation potentials, however, non-conjugated dithiafulvenes are typically oxidized at between E^{ox} +0.9 and +1.4 V. Electron-sufficient and deficient substituents on the dithiafulvenes also affect the potentials.
- (iv) Dithiafulvenes undergo attack by electrophiles at the exocyclic carbon to give 6-substituted derivatives.⁴

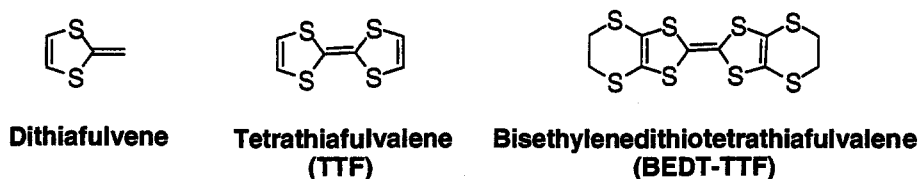


Figure 1. π -Electron donors based on dithiafulvene

In the chemistry of the dithiafulvenes, especially the focus has been centered on derivatives of tetrathiafulvalene (TTF)⁵ containing two 1,3-dithiole rings in conjugation, since the discoveries of a high electrical conductivity in a chloride salt of TTF⁶ and metallic behavior in the charge-transfer (CT) complex with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).⁷ These crystalline materials are composed of stable segregated stacks of the π -donors and counter-anions. Charge-delocalizations throughout the column structures induce short interplanar distances, giving rise to efficient interactions between neighboring π -molecular orbitals, consequently, a high anisotropic conductivity along the direction of stacking through intermolecular intra-stack migration of aromaticity.⁸

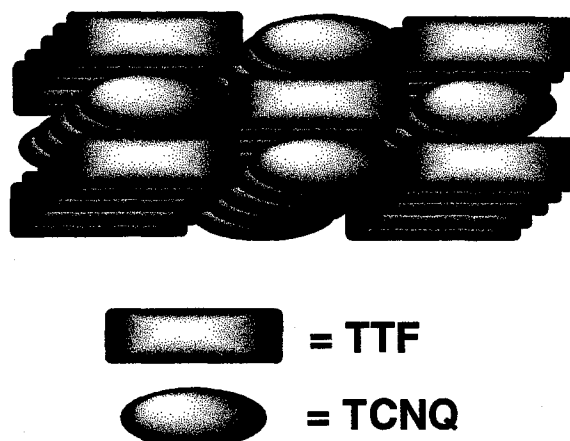


Figure 2. Stacking formation of TTF-TCNQ complex

Despite the inherent electronic advantages of the dithiafulvenes, the donors have two serious problems. The first one is that their CT complexes and radical cation salts tend to be brittle and unprocessable. This can be improved by the incorporation of the dithiafulvenes into polymeric backbones that are well known for their good processability and film-forming property. Several attempts to incorporate the donor units into main-chain or side-chain of polymers have been achieved to prepare formations of good processable CT complexes.⁹ The second one is that some dithiafulvene-based conductors, especially TTF, behave as quasi-one-dimensional metals because of their highly-ordered stacks. Such low-dimensional conductors have been predicted by Peierls to undergo a lattice distortion at low temperatures resulting in a metal-insulator transition.¹⁰ To overcome this issue, modifications of the dithiafulvenes to produce new conductors of higher dimensionality have been intensively studied.¹¹ Conjugation-extended donor molecules containing an extended π -framework between the dithiafulvene moieties are expected as promising electron donors for the organic metals, since the extended conjugation decreases the intramolecular Coulomb repulsive energy between the donor units and hence increases the stability of the oxidation states to enhance intramolecular and interstack interactions (increased dimensionality).¹² An increase of the sulfur content in the structure is also effective to achieve the high dimension. Bisethylenedithiotetrathiafulvalene (BEDT-TTF)¹³ contains extra chalcogen atoms, which can participate in interstack as well as intrastack interaction. The peripheral ethylene units of BEDT-TTF are flexible allowing the molecule to adopt a variety of different conformations. Most BEDT-TTF CT salts are found to be quasi-two-dimensional compounds and some partially oxidized salts have shown ambient-pressure superconductivities up to *ca.* 12K.¹⁴

π -Conjugated Polymeric Systems Containing the Dithiafulvenes

A hybrid system between the dithiafulvene derivatives and π -conjugated polymers is interesting. Many kinds of the π -conjugated polymers have been synthesized and studied extensively for a past few decades owing to their linear π -electron delocalization systems extending over a large number of recurrent units.¹⁵ The dithiafulvene derivatives and the π -conjugated polymers are representative examples of the main two classes of the organic metals. Although these two classes of the materials differ in many respects, the association of some of their structural

characters and properties may contribute to mutual fertilization by development of new materials of both fundamental and technological interest. The conjugated polymers are basically low dimensional conductors, similarly to the TTF CT salts. An incorporation of the donor units into the conjugated polymers would increase the dimensionality of the conduction process in the CT state, due to improved electron mobility along the polymer backbone via π -conjugation, as well as along the stacking direction via π -orbital overlap.¹¹ Furthermore, the donor polymer constitutes a highly polarizable species due to the large number of sulfur atoms in the structure. Therefore, inter- and intramolecular Coulombic repulsions between the charged species would be suppressed, resulting in enhanced stacking CT formations. The processability of the resulting polymer CT salts, needless to say, is better than single CT salts.

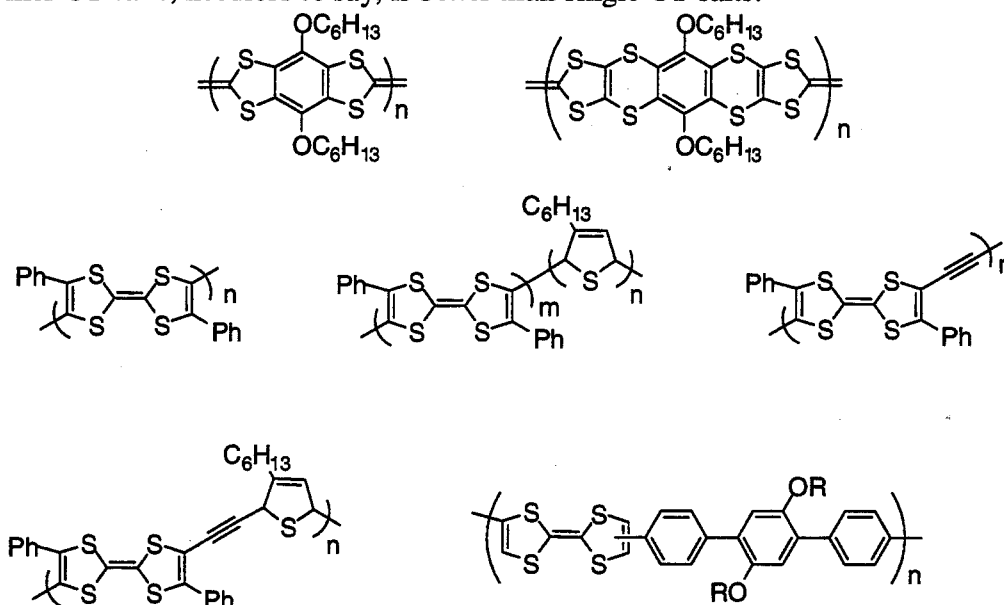
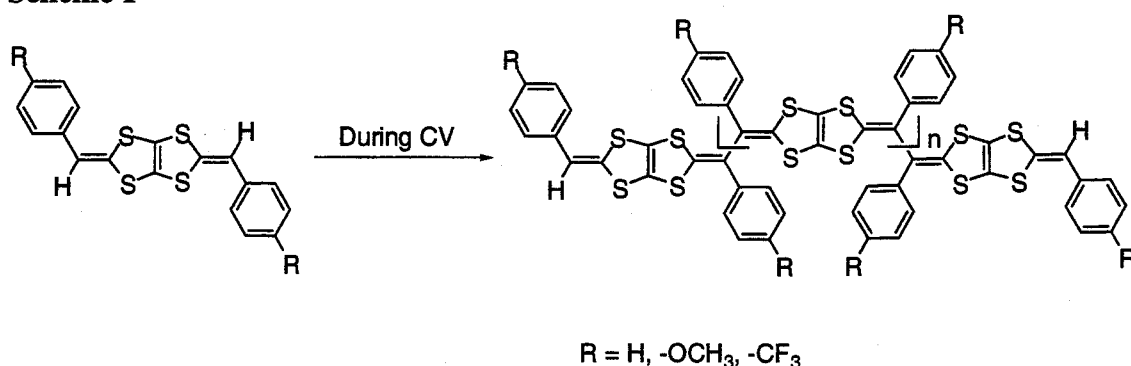


Figure 3. π -Conjugated TTF main chain polymers

Scheme 1



Since the first polymer containing the TTF moiety was prepared via a polycoupling process,^{9a} a lot of attempts to incorporate such donor molecules into a polymeric framework have been carried out. Although some of them showed semiconducting properties upon doping, they were generally disordered or poorly characterizable materials. Progress in synthetic chemistry of the dithiafulvene derivatives during the past decade has allowed the preparation of new polymeric donor systems. In particular, fully conjugated polymers with TTF unit in the main chains

have been reported by several groups.¹⁶ Yamamoto et al. reported the Ni- and Pd-promoted polycondensations and copolymerizations giving π -conjugated TTF polymers.^{16c} Among the polymers, the poly(aryleneethynylene) type polymers had effectively expanded π -conjugation systems due to $\text{C}\equiv\text{C}$ spacer groups and were active for both chemical and electrochemical oxidations, even though they contained electron-withdrawing $\text{C}\equiv\text{C}$ group. The oxidation of di(benzylidene)tetrathiapentalenes in CV resulted in the stepwise formation of linearly extended TTF polymers (Scheme 1).¹⁷ The polymerizations involved as a first step the formation of the monomer radical cations which underwent rapidly radical dimerization reactions to produce dicationic protonated TTF derivatives. The dicationic intermediates deprotonated slowly to stable vinylogous TTF polymers. Unfortunately, all the TTF main chain polymers above mentioned did not form CT complexes with organic acceptors.

Polymerization of 2-ethynyl-TTF by use of a rhodium catalyst produced a TTF-side chain polyacetylene.¹⁸ The polymer itself showed a low electrical conductivity ($<1 \times 10^{-9}$ S/cm). The polymer reacted to give CT complexes with various electron acceptors such as TCNQ, tetrafluorotetracyanoquinodimethane (TCNQF_4), dichlorodicyanoquinone (DDQ), and iodine. Among them, the CT complex with TCNQ (TTF unit : TCNQ = 5 : 1) showed the highest conductivity of 2.1×10^{-3} S/cm.

Dithiafulvenes as Building Blocks in Supramolecular Chemistry

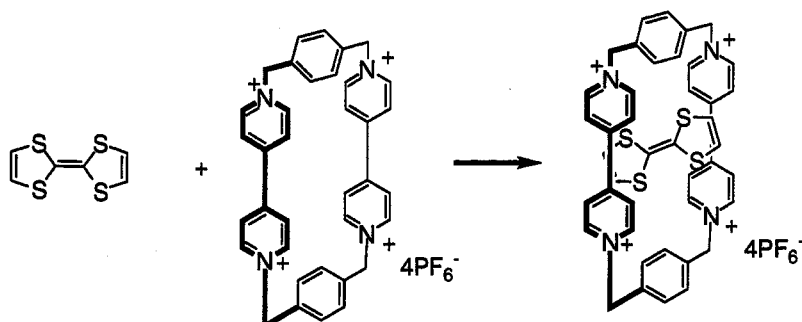
The dithiafulvene derivatives have been utilized not only for components of the molecular conductor but also π -rich redox active building blocks.^{2c,19} The reversible redox and intermolecular CT properties of the donors are attracting attention in the context of molecular/supramolecular systems which are prototype nanoscale devices. For example, dendritic polymers based on TTF have been synthesized and studied extensively by Bryce and coworkers with an aim of accomplishing controlled and reversible multi-redox systems.²⁰ Another interesting application implicates crown-annelated TTFs, in which the crown ether moiety is located at the dithiole rings, as complexing agents for the recognition of metal ions.²¹ Development in synthetic dithiafulvene chemistry during the past decade has allowed the preparation of a number of such elaborate molecular systems.

The covalent linkage of dithiafulvene derivatives to π -acceptor moiety through a σ - or π -bonded bridge^{2b} offers considerable potential for the study of intramolecular CT processes. Systems of this general type are central to studies on chromophores for dyes, single component conductors, nonlinear optical properties, synthetic light harvesting systems and theoretical aspects of charge transport at molecular level.²²

Mechanically interlocked molecular compounds, including catenanes, rotaxanes, and carceplex, are constituted of molecules composed of two or more components that cannot be separated from each other.²³ The development of strategy for achieving controlled self-assembling systems by non-covalent interaction enables to prepare such attractive compounds for applications in nanoscale molecular devices. Stoddart and coworkers reported that a macrocyclic bisviologen acceptor acts as a versatile host for π -electron rich systems, such as diphenol methyl ethers, dinaphthol methyl ethers and aromatic amino acids.²⁴ They also discovered that TTF and the

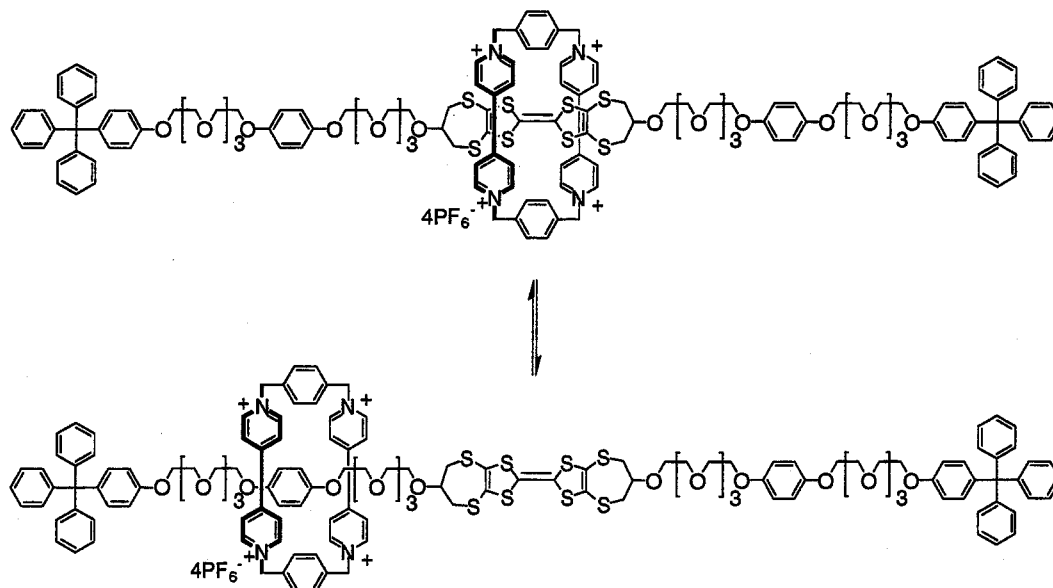
acceptor form a 1:1 complex in which TTF is located within the cavity of the acceptor (Scheme 2).²⁵ Since the discovery, some interlocked and intertwined molecules (e.g. catenanes and rotaxanes) based on the TTF units have been synthesized.²⁶ They acted as chemically- and electrochemically-switches at the molecular level.

Scheme 2



A polyrotaxane containing two electron-donating sites (TTF and hydroquinone moieties) as stations in the polymer backbone showed that the incorporated cyclic acceptor moves by external stimuli and possibly two translational isomers would exist (Scheme 3).²⁷ The ratio between two isomers was solvent dependent, with a preference however for the hydroquinone moiety. In the CV measurement, the cyclic acceptor moved from TTF to hydroquinone moiety along the chain upon oxidation of the TTF unit.

Scheme 3



New Application of Thioketene Dimers to π -Electron Donors

There is a long-standing interest in the chemistry and the properties of cyclic compounds containing sulfur atom in modern material chemistry due to their redox chemistry. Especially, the focus has been on dithiole derivatives, e.g. dithiafulvenes and TTFs, since the finding of metallic conductivity and low temperature superconductivity in radical cation salts. The quite low oxidation potentials of 1,4-

dithiin compounds have been reported, recently.²⁸ On the other hand, the reactivity of thioketenes shows features of the analogous ketene chemistry.²⁹ The most common example of (2+2) cycloadditions between thioketenes and C=S compounds is dimerization of thioketenes to give 2,4-bis(alkylidene)-1,3-dithietanes, which have been known for more than 100 years.³⁰ Although the basic structure of the dimer compounds is similar to that of the dithiafulvene derivatives, no research on the electric and magnetic property of the thioketene dimers has been reported up to date. The potential electronic property of the thioketene dimer moiety is considerably attractive with the aim of application to a new and better π -donor.

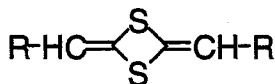


Figure 4. Structure of a thioketene dimer

Survey of This Thesis

Thioketenes are usually considered as highly reactive and short-lived species similar to their ketene analogs.²⁹ The development of the ketene chemistry has resulted in utilizations of ketenes and bisketenes for monomers in several different types of polymerizations.³¹ Although understanding of the reactions of thioketenes has been highly improved within last several decades, the direct use of thioketenes in polymer synthesis has been very limited to date. In this thesis, the author describes the syntheses of new polymers with electron donating thio-cyclic compounds by use of cycloaddition polymerizations of thioketenes. The resulting polymers showed interesting optical, electrochemical and conducting properties.

Part I deals with the syntheses of novel poly(dithiafulvene)s by cycloaddition polymerizations of aldothioketenes and their alkynethiol tautomers. Formations of the polymer CT complexes are also described. In Chapter 1, π -conjugated poly(dithiafulvene)s are synthesized from aromatic diynes. Efficient expansions of π -conjugation systems in the polymers are evident from their UV-vis absorption spectra. The CV analysis of the polymers shows that the polymers behave as strong electron donors. Chapter 2 demonstrates that the poly(dithiafulvene) forms soluble CT complex with TCNQ. The stoichiometries of the CT complex are the dithiafulvene repeating unit/TCNQ = 1/1. Electrical conductivity of the polymer is highly improved after formation of the CT complex. Investigation of π -conjugated poly(dithiafulvene)s with typical heteroaromatic units (thiophene and pyridine moieties) is described in Chapter 3. Incorporation of the heteroaromatic units gives the more effective conjugations than those of aromatic poly(dithiafulvene)s. The alternating copolymer of the dithiafulvene with pyridyl units shows a high intrinsic conductivity due to the intramolecular CT structure. Comparison of chemical and physical properties between π -conjugated poly(dithiafulvene)s and poly(diselenafulvene)s is carried out in Chapter 4. The poly(diselenafulvene)s are prepared by cycloaddition polymerizations of selenoketenes. Effects of side alkyl chains on the polymers are also demonstrated. Chapter 5 describes the synthesis of non-conjugated poly(dithiafulvene)s in which the aromatic moieties are bridged by oxygen, methylene and alkylene units. The properties of the polymers are different from those of the conjugated poly(dithiafulvene)s.

Part II shows preparations of poly(dithiafulvene)s toward intelligent

functional materials. In Chapter 6, an alternating π -conjugated copolymer of ferrocene with dithiafulvene shows a unique redox property due to an effective interaction between the different donors in the polymer. A poly(dithiafulvene) having 2,2'-bipyridyl unit gives a formation of ruthenium complex in Chapter 7. Cyclic voltammogram of the complex shows redox peaks, which are characteristic of the dithiafulvene unit and the tris(bipyridyl) ruthenium complex. The bipyridyl-poly(dithiafulvene) exhibits high electrical conductivity owing to the intramolecular CT structure. In Chapter 8, the author shows that a low molecular dithiafulvene is inserted into the cavity of a cyclic acceptor creating a 1:1 complex as a pseudorotaxane formation by a CT interaction, similarly to TTF. The π -conjugated poly(dithiafulvene) also gives a pseudopolyrotaxane formation with the acceptor. Such hybrid system shows interesting electronic and conducting properties, hence, will find the application in the macromolecular, supramolecular and material fields of chemistry. In Chapter 9, a new conjugation polymeric system between π unit and saturated σ chain is achieved by the combination of pyridinium moiety and polymethylene chains, in addition, incorporation of intramolecular charge-transfer structure (pyridinium-dithiafulvene-pyridinium) into the π unit enhances the σ - π conjugation. Usually polymethylene spacer units inevitably act as interrupters of conjugative effects between π -units, however, use of the intramolecular CT effect induced by the dithiafulvene shows efficient σ - π conjugations between the polymethylene chains and the π -units.

Part III describes new syntheses of conjugated polymer materials containing the thioketene dimer unit in the structures. The author has prepared π -conjugated polymers with the thioketene dimer unit in Chapter 10. These are the first polymers containing the thioketene moiety in the structure. The electron donating properties of the poly(thioketene dimer)s are confirmed by cyclic voltammetry and are found to be stronger than those of the poly(dithiafulvene)s. Interestingly, the poly(thioketene dimer)s form conducting CT complexes with TCNQ, indicating new candidates as organic conductors instead of the materials based on the dithiafulvenes. A series of silyl and disilyl substituted thioketene dimers, including polymers, are synthesized in Chapter 11. The study demonstrates an interesting fact that direct attachment of the thioketene dimer to the Si-Si bond affords intramolecular CT from the thioketene dimer unit to the Si-Si moiety, even though the Si-Si unit has been regarded as an electron donor so far. Expansion of σ - π conjugation in a polymeric system enhances the CT interaction efficiently.

Approaches toward the functional macromolecules with the electroactive thio-cyclic units are performed in this thesis. The conjugated poly-donor molecules are synthesized to combine the processability with the significant electron-donating properties of the dithiafulvene systems. All of them formed CT complexes with organic acceptors, such as TCNQ, achieving higher conductivities and conducting dimensionalities. The high electron-donating ability of the dithiafulvenes is exploited in a rotaxane system, to be utilized for a sensor, a molecular switch and a device. This thesis also describes that the electronic properties of the thioketene dimers is hopeful, similarly to the dithiafulvene derivatives. The electron-donating ability of the thioketene dimer was revealed to be fairly strong and can be applied to the various unique electronic systems.

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Part I

Preparation of Conjugated Poly(dithiafulvene)s

Chapter 1

π -Conjugated Poly(dithiafulvene)s by Cycloaddition Polymerization of Aldothioketenes with Their Alkynethiol Tautomers Derived from Aromatic Diynes

Abstract: π -Conjugated polymers (**2**) having electron-donating dithiafulvene units in the main chain were prepared by the addition reaction of aldothioketenes derived from π -conjugated diynes (1,4-diethynylbenzene, 4,4'-diethynylbiphenyl, 2,7-diethynylfluorene, and 1,3-diethynylbenzene) with their alkynethiol tautomers. The structures of the polymers were supported by IR and ^1H NMR spectra, and elemental analysis. The obtained polymers were soluble in DMSO and DMF, and partially soluble in acetone and methanol. The absorption peak due to the π - π^* transition of **2a** (prepared from 1,4-diethynylbenzene) was largely bathochromic shifted in comparison with that of 2-benzylidene-4-phenyl-1,3-dithiole (**3**) as a model compound. This red-shift is ascribed to an effective expansion of the π -conjugation system in **2a**. In the case of **2d** (prepared from 1,3-diethynylbenzene), the absorption maximum was same as that of **3**. This result was caused by the fact that the π -conjugation is not expanded through 1,3-disubstituted benzene. The cyclic voltammograms show that an anodic shift and a broadening of the oxidation peak for the dithiafulvene unit for **2a** was observed compared with that of **3**. Before doping, **2a** exhibits an electrical conductivity of 3×10^{-7} S/cm as measured on a cast film from 1,3-dimethyl-2-imidazolidinone. Oxidation with iodine raised the electrical conductivity of 1×10^{-3} S/cm.

Introduction

Derivatives of dithiafulvene, including tetrathiafulvalenes (TTF), act as electron donors and form stable charge-transfer complexes and radical ion salts with a wide range of organic and inorganic acceptor species.¹ These molecules are components of organic metals. Since the first polymer containing a TTF moiety was prepared via a polycoupling process,² several attempts to incorporate such donor molecules into a polymeric framework have been carried out.³⁻⁷ Polymers containing dithiafulvene units were prepared by polymerization of vinyl derivatives^{4a} or polycondensation of substituted dithiafulvenes with diacid chlorides, *p*-phenylene diisocyanate, and terephthalaldehyde.^{4b}

In a π -conjugated polymer having derivatives of dithiafulvene, not only the processability of charge-transfer salts can be improved but the dimensionality of the conduction process can be increased in the doped state, due to the electron mobility along the polymer backbone via π -conjugation, as well as along the stacking direction via π -orbital overlap.^{1a,5} Examples of polymers containing dithiafulvene derivatives in the π -conjugated main chain have been limited, however. Müllen et al. have prepared a fully conjugated structure by inserting a TTF moiety in the conjugated backbone.⁶ Yamamoto et al. reported a preparation of soluble π -conjugated polymers containing TTF units in the π -conjugated main chain by Pd-promoted polycondensations.⁷

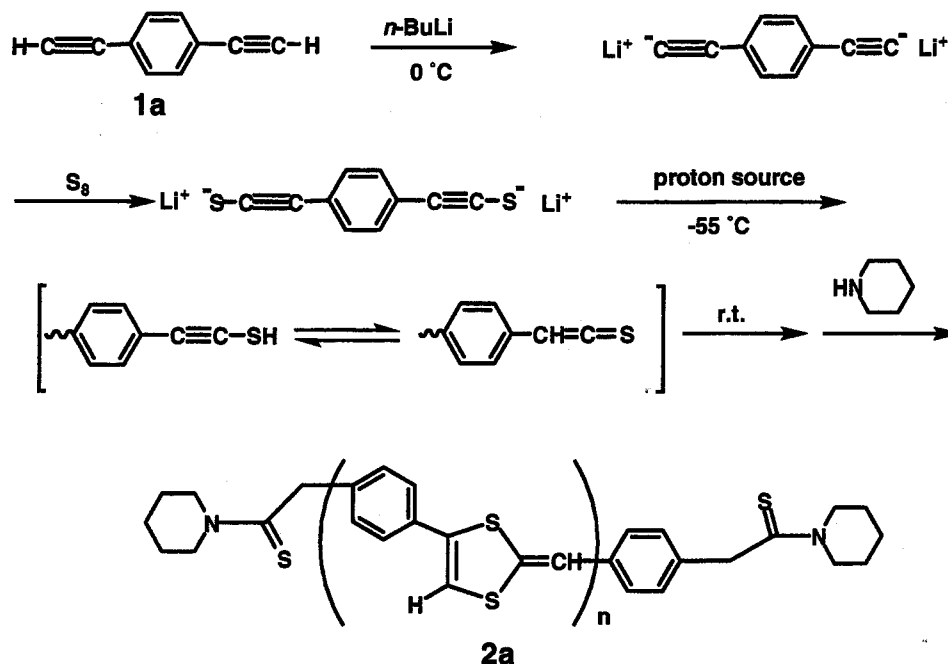
Among numerous preparation methods, thioketenes can be derived from alkynyl thiolates.⁸ Alkynyl thiolates can be regarded as aldothioketene anions, and are accessible via addition of sulfur to acetylide anions. Protonation of alkynyl thiolates yields the thiols which tautomerize to aldothioketenes. The usual result of the reaction between aldothioketenes and their alkynethiol tautomer is the formation of dithiafulvenes.⁹ Thioketenes are highly reactive and short-lived species similar to their ketene analogs.¹⁰ The chemistry of ketenes has been developed since the beginning of this century and ketenes and bisketenes can be used as the monomer in several different types of polymerizations.¹¹ Although understanding of the reactions of thioketenes has been highly improved within last several decades, the direct use of thioketenes in polymer synthesis has been very limited to date. In this Chapter 1, the author reports the synthesis and properties of π -conjugated polymers having electron-donating dithiafulvene units in the main chain by a cycloaddition polymerization of an aldothioketene derived from aromatic diyne monomers with their alkynethiol tautomers.

Results and Discussion

The cycloaddition polymerization of the aldothioketene derived from 1,4-diethynylbenzene was carried out as follows (Scheme 1). After Et₂O solution of 1,4-diethynylbenzene (**1a**) was treated with *n*-butyllithium, powder of sulfur was added to the solution. Protonation of the resulting alkynyl thiolate was performed by adding an equimolar amount of water to the mixture at -55 °C. The temperature of the mixture was allowed to rise to room temperature and the reaction mixture was stirred for 3 h to effect polymerization. Finally, piperidine was added to the mixture to quench terminal thioketenes. The mixture was then poured into a large quantity of Et₂O. The precipitate was washed with Et₂O several times to remove unreacted piperidine, followed by washing with water to remove inorganic salts. After drying under reduced pressure, an orange polymer (**2a**) was obtained in 76 % yield. Polymer **2a** was soluble in DMSO and DMF, and partially soluble in acetone and methanol. Polymer **2a** was

dissolved in DMSO and was subjected to GPC measurement. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of the polymer were $M_n = 11,000$ and $M_w/M_n = 1.22$, respectively.

Scheme 1



The structure of **2a** was confirmed by IR and ^1H NMR spectroscopies compared with those of model compounds. 2-Benzylidene-4-phenyl-1,3-dithiole (**3**)^{9a}, that was quantitatively obtained by the treatment of lithium 2-phenylethynethiolate with water in Et_2O , was used as a model compound for dithiafulvene unit. An almost quantitative model compound for the terminal thioamide (**4**) was also obtained from lithium 2-phenylethynethiolate with an excess of piperidine. The reaction between a thioketene and a secondary amine is a very efficient process and appears to be quantitative.^{8b,c, 10} The IR spectrum of polymer **2** showed a strong peak at 1578 cm^{-1} due to a $\text{C}=\text{C}$ vibration of the dithiafulvene unit. The IR spectrum also showed peaks at 1502 and 1256 cm^{-1} , which were assigned to the terminal thioamide group. The ^1H NMR spectrum of **2a** was similar to that of the model compounds. In the ^1H NMR spectrum of **2a** (Figure 1c), a broad peak for the benzylidene proton appeared at 6.7 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.2 ppm. In the ^1H NMR spectrum of **4** (Figure 1b), two triplets (4.28 and 3.57 ppm) assigned to $\text{N}-\text{CH}_2$ - appeared due to hindered rotation around the $\text{C}-\text{N}$ bond.^{9b,c} The peak at 4.35 ppm was assigned to $\text{Ph}-\text{CH}_2-\text{C}(=\text{S})-\text{N}$ in **4**. The ^1H NMR spectrum of **2a** also shows two broad peaks at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. Comparison of the intensities of the absorptions of the dithiafulvene protons in the repeating unit with those of the absorptions of the terminal thioamide protons resulted in the estimation of number-average degree of polymerization (DP) as 26 ($M_n=5440$). This value should be more reliable than that from GPC data.

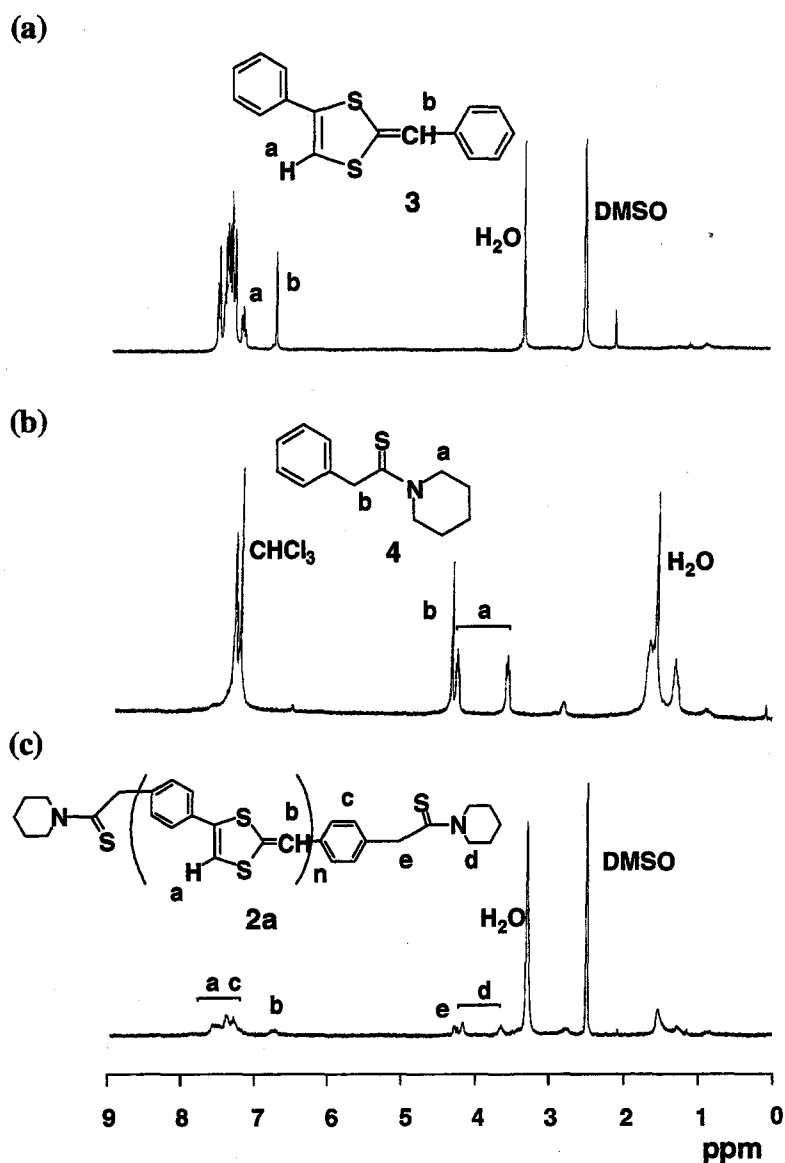
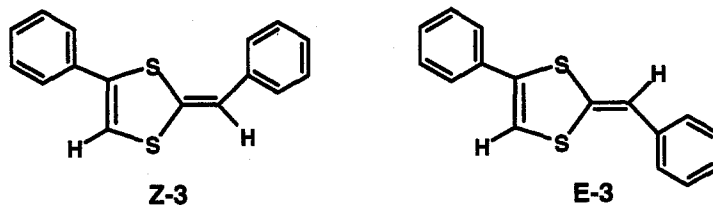


Figure 1. ^1H NMR spectra of (a) **4** in $(\text{CD}_3)_2\text{SO}$, (b) **3** in CDCl_3 , and (c) **2a** in $(\text{CD}_3)_2\text{SO}$.



Although the ^{13}C NMR spectrum of the polymer **2a** was not clearly obtained due to its low solubility, peaks around 113 ppm assigned to $\text{Ph}-\text{CH}=\text{C}<$ and $\text{S}-\text{CH}=\text{C}(\text{Ph})-\text{S}$ of the dithiafulvene unit can be recognized. The ^{13}C NMR spectrum of

the model compound **3** shows a major peak at 114.00 ppm and a minor peak at 113.55. The former and the later peaks are assigned to Ph-CH= in the Z and the E isomers of **3**, respectively.¹² Comparison of the peak areas shows that **3** was a mixture of Z (94 %) and E isomers (6 %). This observation indicated that a major structure of the repeating unit for the polymer **2a** might be a Z configuration.


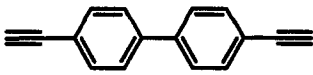
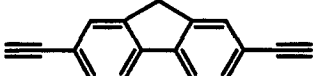
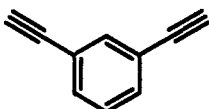
Table 1. Synthesis of Poly(dithiafulvene)s

entry	proton source	solvent	polymerization time (h)	yield (%)	M_n^c
1	H ₂ O	Et ₂ O	3	93	5440
2	H ₂ O	THF	3	65	1980
3	H ₂ O	toluene	3	32	1640
4	H ₂ O	Et ₂ O	6	99	4680
5	H ₂ O ^a	Et ₂ O	48	no ^b	-
6	<i>t</i> -BuBr	Et ₂ O	48	no ^b	-

^a An excess amount of H₂O was added. ^b No polymeric product was obtained.

^c Determined from ¹H NMR.

Table 2. Synthesis of Poly(dithiafulvene)s Using Various Aromatic Diynes^a

diynes	polymer	yield(%) ^b	M_n^c	UV λ_{max} (nm) ^d
	2a	76	5440	398
	2b	55	1830	379
	2c	66	2810	401
	2d	54	3980	359

^a Polymerizations were carried out in Et₂O at room temperature for 3 h. ^b Isolated yields after washing with water. ^c Determined from ¹H NMR. ^d Absorption spectra were recorded in diluted acetonitrile solutions at room temperature.

The results of the polymerization conducted under various conditions are summarized in Table 1. Further polymerization time for 6 h in Et₂O did not increase the molecular weight of the polymer (entries 1 and 4). The use of other solvents such as THF and toluene also decreased both the molecular weight and the yield of the polymers (entries 2 and 3). In preparation of thioamides from alkynyl thiolates and secondary amines, it was reported that favorable results were obtained when *t*-butyl bromide was used as a proton donor.^{8b} However, entry 6 shows that ideal polymerization did not proceed even after 48 h when *t*-butyl bromide was used instead of water in this system. Although the model compound **3** was obtained in good yield after addition of a large amount of water to the alkynyl thiolate solution,^{9a} adding an

excess amount of water did not give the polymeric product (entry 5). The polymerization was inhibited by addition reaction of water to thioketene.

Thermogravimetric analysis (TGA) was recorded for **2a** under nitrogen. The small weight loss of the polymer started at 250 °C. Subsequently, a rapid weight loss began at about 430 °C and completed at 540 °C. This relatively high thermal stability suggests potential utility of the present materials as in electronic devices.

The results of the polymerization with various diyne monomers are summarized in Table 2. In every case, the corresponding polymers were obtained in good yields. The relatively low molecular weights of **2b** and **2c** are probably due to the low solubility of the polymer products. The structures of the polymers were supported by IR and ¹H NMR spectra, and elemental analysis.

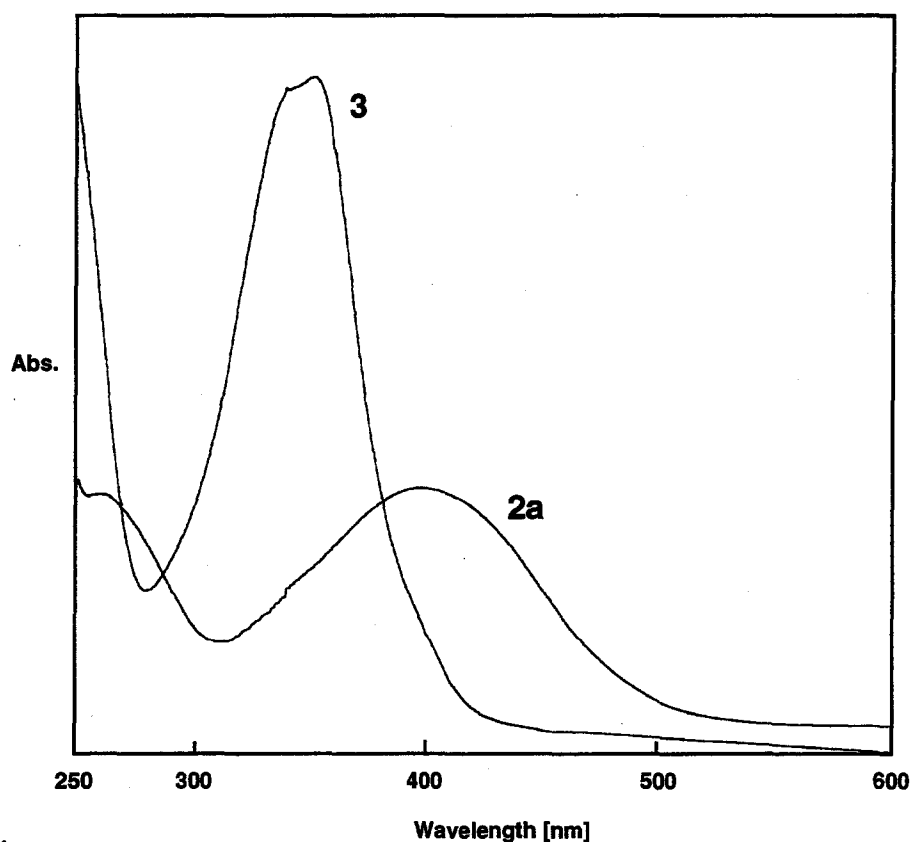


Figure 2. UV-vis spectra of **2a** and **3** in acetonitrile.

In the UV-vis absorption spectral data for the diluted acetonitrile solutions of **2a-d** are also shown in Table 2. Figure 2 shows the spectrum of **2a**, in which the peak due to the π - π^* transition of the polymers was observed at 398 nm. The value was largely bathochromic shifted in comparison with that of the model compound **3**. This red-shift is ascribed to an effective expansion of the π -conjugation system in **2a**. The smaller bathochromic shift of **2b** from the λ_{max} of **3**, compared with the bathochromic shifts observed with **2a** and **2c**, was due to a steric distortion of the biphenyl moiety. In the case of **2d**, the absorption maximum was same as that of **3**. This result was caused by the fact that the π -conjugation is not expanded through 1,3-disubstituted benzene.

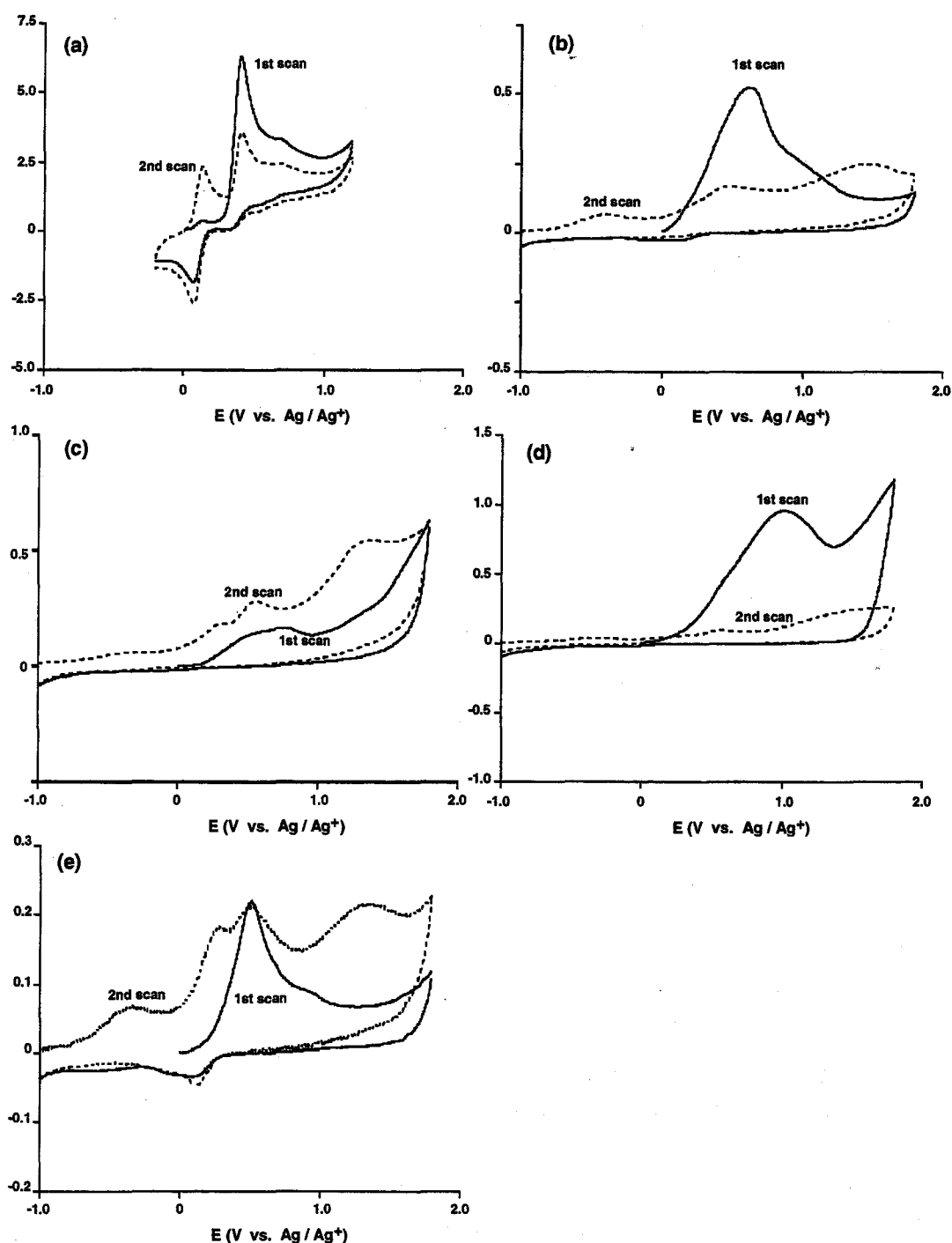


Figure 3. Cyclic voltammograms of (a) **3**, (b) **2a**, (c) **2b**, (d) **2c**, and (e) **2d**. Measured in CH_3CN solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 300 mV/s.

In order to elucidate the redox properties of the polymer, cyclic voltammetry measurements were carried out. As shown in Figure 3b, the cast film of **2a** gave a single-broad oxidation peak at about 0.61 V vs. Ag/Ag^+ . 2-Benzylidene-4-phenyl-1,3-dithiole (**3**) as a model compound for **2** showed a single oxidation peak at 0.40 V vs.

Ag/Ag⁺ (Figure 3a). An anodic shift of the oxidation potential for the dithiafulvene unit in **2a** was observed compared with that of **3**. It clearly indicated that the dithiafulvene unit incorporated in the π -conjugated system caused stabilization against oxidation. In cyclic voltammograms of simple one-electron reversible redox reactions, the potential difference ($\Delta E_{p/2}$) between the oxidation peak (E_{ap}) and the half-peak potential ($E_{p/2}$) was 56.5 mV. The 1st oxidation peak of the model compound **3** gives potential difference ($\Delta E_{p/2}$) of 55 mV, whereas that of the polymer **2a** gives 295 mV. An apparent broad oxidation peak for **2a** compared with that of **3** suggested the interaction between dithiafulvene units along the π -conjugated polymer main chain. Such anodic shift and broadening of the peak have been reported for several electrochemically active π -conjugated polymers.¹³

Table 3. Oxidation Potentials and half-peak Potentials of Poly(dithiafulvene)s^a

polymer	E_{pa} (V)	$E_{p/2}$ (V)	$\Delta E_{p/2}$ (V) ^b
2a	0.610	0.315	0.295
2b	0.755	0.350	0.405
2c	1.005	0.597	0.408
2d	0.504	0.315	0.136
model compound 3	0.402	0.347	0.055

^a Measured in CH₃CN solution of 0.1 M [NEt₄]BF₄ at 300 mV/s. ^b Potential difference between oxidation peak (E_{ap}) and half-peak potential ($E_{p/2}$).

The cast film of **2b-d** also gave single oxidation peaks. Oxidation potentials (E_{pa}) and half-peak potentials ($E_{p/2}$) of the polymers are summarized in Table 3. The oxidation peaks of **2b** and **2c** were largely anodic shifted and broadening in comparison with that of **3**. The fairly higher oxidation potential of **2c** than that of **2b** was due to a plane configuration of the fluorene unit. As shown in Figure 3e, the oxidation peak of **2d** was contrast to those of **2a-c**. The peak potential difference and the degree of broadening of **2d** are small, suggesting the electron exchange between dithiafulvene units through 1,3-disubstituted benzene was not effective.

As shown in Figure 3a, during the reverse cathodic scan, a reversible wave appears at a less positive potential of the irreversible oxidation peak (E_{ap} = 0.40 V). This new redox system was due to a dimer product of the dithiafulvene. In the literature, oxidative dimerization of dithiafulvenes has been known to form TTF vinylogues.¹⁴ In cyclic voltammograms of **2a** and **2d**, reversible redox peaks appeared after the irreversible oxidation peaks were scanned. These results show that the oxidation of the polymers led to an inter- and/or intra-molecular dimerization of the dithiafulvene unit.

Before doping, **2** exhibits an electrical conductivity of 3×10^{-7} S/cm as measured on a cast film from 1,3-dimethyl-2-imidazolidinone. Oxidation with iodine raised the electrical conductivity of 1×10^{-3} S/cm, four orders of magnitude greater than the undoped polymer.

Summary

In conclusion, the author has prepared new π -conjugated polymers with electron donating dithiafulvene unit in the main chains by cycloaddition

polymerizations of aldothioketenes with their alkynethiol tautomers derived from aromatic diynes. The π -conjugation systems of the polymers were effectively expanded without the 1,3-substituted polymer **2d**. The electrochemistry of the polymers was investigated by CV analysis. After doped with iodine, the electrical conductivity of the polymer **2a** showed 1×10^{-3} S/cm.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2 . 4,4'-Diethynylbiphenyl, 2,7-diethynylfluorene, and 1,3-diethynylbenzene were synthesized according to the literature.¹⁵

Measurements. 1H , ^{13}C NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument ($10^\circ C/min$). Gel permeation chromatography was carried out on Shodex K-803 plus K-804 columns by using DMSO as an eluent at $50^\circ C$ after calibration with standard poly(8-oxa-6-azabicyclo[3.2.1]octan-7-one) samples. For cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit. The polymer film (thickness = about $7.6 \mu m$) was prepared by dropping of 5 wt% 1,3-dimethyl-2-imidazolidinone/THF (1/1, w/w) solution onto glass plates equipped with gold electrodes, followed by drying at $50^\circ C$ for 1 h and $120^\circ C$ for 0.5 h. I_2 -doping was carried out by contacting the polymer film with gaseous I_2 under vacuum.

Polymerization. A typical experimental procedure is as follows. To a solution of 1,4-diethynylbenzene (126 mg, 1.00 mmol) in Et_2O (1.0 mL), 1.6 M solution of *n*-butyllithium in hexane (1.25 mmol, 2.00 mmol) was added at $0^\circ C$. After stirring for 0.5 h, the powder of sulfur (64 mg, 2.00 mmol) was added to the solution. The reaction mixture was stirred for 2 h, then cooled at $-55^\circ C$ and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.3 mL) and stirred for 0.5 h. The mixture was then poured into a large quantity of Et_2O . The obtained precipitate was washed with Et_2O for several times to remove unreacted piperidine, followed by washing with water to remove inorganic salts. After drying under reduced pressure, an orange-colored polymer was obtained.

2a. Yield: 153 mg (76 %). 1H -NMR (δ , ppm): 1.2-1.6 (CH_2 of piperidine unit), 3.6 ($N-CH_2$ of piperidine unit), 4.2 ($N-CH_2$ of piperidine unit), 4.3 ($CH_2C(=S)N<$), 6.7 ($>C=CH-Ph$), 7.1-7.7 (aromatic and 1,3-dithiole ring protons); IR (KBr, cm^{-1}) 2928, 1578, 1540, 1502, 1493, 1290, 1256. Anal. Calcd: C, 63.07; H, 4.10; N, 1.44; S, 31.39. Found: C, 63.09; H, 4.45; N, 1.50; S, 30.96.

2b. 1H -NMR (δ , ppm): 1.2-1.6 (CH_2 of piperidine unit), 3.6 ($N-CH_2$ of piperidine unit), 4.2 ($N-CH_2$ of piperidine unit and $CH_2C(=S)N<$), 6.8 ($>C=CH-Ph$), 7.1 (1,3-dithiole ring proton), 7.2-7.8 (aromatic); IR (KBr, cm^{-1}) 2918, 1578, 1534, 1500, 1491, 1247.

Anal. Calcd: C, 72.05; H, 4.67; N, 1.47; S, 21.96. Found: C, 72.82; H, 4.39; N, 1.42; S, 20.97.

2c. $^1\text{H-NMR}$ (δ , ppm): 1.3-1.7 (CH_2 of piperidine unit), 3.4 (N-CH_2 of piperidine unit), 4.0 (CH_2 of fluorene unit), 4.2 (N-CH_2 of piperidine unit and $\text{CH}_2\text{C(=S)N<}$), 6.8 ($>\text{C=CH-Ph}$), 7.2-8.1 (aromatic and 1,3-dithiole ring protons); IR (KBr, cm^{-1}) 2934, 1567, 1558, 1504, 1479, 1283, 1259. Anal. Calcd: C, 73.14; H, 4.17. Found: C, 74.97; H, 4.30.

2d. $^1\text{H-NMR}$ (δ , ppm): 1.1-1.6 (CH_2 of piperidine unit), 3.6 (N-CH_2 of piperidine unit), 4.2 (N-CH_2 of piperidine unit and $\text{CH}_2\text{C(=S)N<}$), 6.7 ($>\text{C=CH-Ph}$), 6.9-7.6 (aromatic and 1,3-dithiole ring protons); IR (KBr, cm^{-1}) 2929, 1574, 1548, 1501, 1480, 1254. Anal. Calcd: C, 63.45; H, 3.61; N, 0.72; S, 32.26. Found: C, 63.69; H, 3.30; N, 1.04; S, 31.96.

2-Benzylidene-4-phenyl-1,3-dithiole (3). The model compound **3** was prepared according to ref. 9a. Mp 204-5 °C (lit.^{4a} Mp 197-199 °C); IR (KBr) 1578, 1556, 1484 cm^{-1} ; $^1\text{H NMR}$ (270 MHz, $(\text{CD}_3)_2\text{SO}$) δ 6.73 ($>\text{C=CH-Ph}$, s, 1H), 7.19 (1,3-dithiole ring proton, m, 1H), 7.30-7.55 (aromatic, m, 10H); $^{13}\text{C NMR}$ (270 MHz, CDCl_3) δ 112.17, 114.00, 125.98, 126.56, 127.03, 128.50, 128.61, 128.72, 132.99, 134.59, 135.56, 137.11.

1-(2-Phenyl-1-thioxoethyl)-piperidine (4). To a solution of piperidine (2.5 ml, 25 mmol) in Et_2O (1 ml) was added 1.56 ml of 1.6 M solution in hexane of *n*-butyllithium (2.50 mmol) at -30 °C. Phenylacetylene (255 mg, 2.50 mmol) was added to the reaction mixture. The temperature of the mixture was allowed to rise to 80 °C. The powder of sulfur (80 mg, 2.50 mmol) was added, and the mixture was stirred for 2 h, and then 1N HCl (5 ml) was added. The brown organic layer was separated, and the aqueous phase was extracted with Et_2O . The combined organic phase was dried over anhydrous MgSO_4 , and evaporated to give the product.; yield 100 %. Mp 69-70 °C (lit.⁹ Mp 71-72 °C); $^1\text{H-NMR}$ (CDCl_3) δ 1.30 (CH_2 , m, 2H), 1.65 (CH_2 , m, 4H), 3.57 (N-CH_2 , t, 2H), 4.28 (N-CH_2 , t, 2H), 4.35 ($\text{CH}_2\text{C(=S)N<}$, s, 2H), 7.33 (aromatic, m, 5H); IR (KBr) 1500, 1458, 1289, 1260 cm^{-1} .

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Chapter 2

Linearly Extended π -Conjugated Poly(dithiafulvene) Formed Soluble Charge-Transfer Complex with 7,7,8,8-Tetracyanoquinodimethane

Abstract: A soluble charge-transfer (CT) complex of π -conjugated donor polymer with 7,7,8,8-tetracyanoquinodimethane (TCNQ) was formed when TCNQ was added to a DMSO solution of a π -conjugated poly(dithiafulvene) (**2**). In DMSO, **2** reacted with TCNQ to produce a dark green solution. After the precipitated TCNQ was filtered, the filtrate was evaporated to obtain a dark green powder. The resulting CT complex was soluble in acetonitrile, DMSO, DMF, acetone, and MeOH, and partially soluble in THF. The UV-vis absorption spectra suggested a formation of the CT complex containing about 1:1 ratio of dithiafulvene unit to TCNQ. The UV-vis absorption and FT-IR analyses indicated that the anion radical of TCNQ was initially formed by the charge-transfer reaction when TCNQ was added to the solution of **2**, and the remaining TCNQ was interacted with **2** as a partially charge-transferred form. In the ^1H NMR spectra, the broad peak attributed to the benzylidene proton of **2** was shifted to a lower magnetic field proportional to the TCNQ feed ratio against the dithiafulvene unit of **2**. The CT complex has a conductivity of $2 \times 10^{-4} \text{ S cm}^{-1}$, three orders of magnitude greater than the uncomplexed polymer.

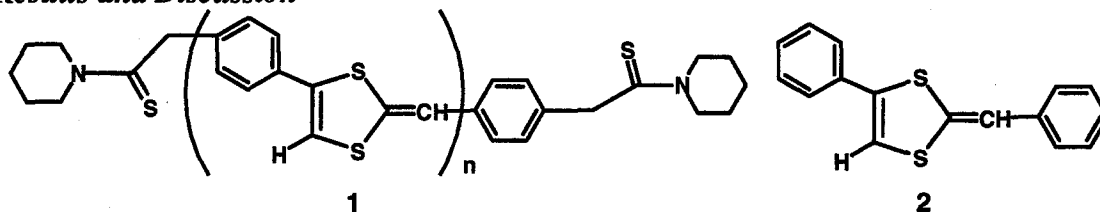
Introduction

Derivatives of dithiafulvene, including tetrathiafulvalenes (TTF), act as electron donors and form stable charge-transfer (CT) complexes and radical ion salts with a wide range of acceptor species such as 7,7,8,8-tetracyanoquinodimethane (TCNQ).¹ The formation of CT complexes by chemical oxidation can be accomplished only if the redox potentials of the donors and acceptors are carefully balanced. The electrical conductivity of the solid state of TTF-TCNQ along the stacking direction is about three orders of magnitude higher than that in the perpendicular direction, and therefore TTF-TCNQ behaves as a quasi-one-dimensional metal. Such low-dimensional conductors have been predicted by Peierls to undergo a lattice distortion at low temperatures resulting in a metal-insulator transition.^{1a}

In the poly-conjugated donor molecule, not only the processability of charge-transfer salts can be improved but the dimensionality of the conduction process can be increased in the doped state, due to the electron mobility along the polymer backbone via π -conjugation, as well as along the stacking direction via π -orbital overlap.² There have been several attempts to incorporate dithiafulvene derivatives into the backbones of polymers,³ examples of polymers containing dithiafulvene units in the π -conjugated main chain have been limited. Müllen et al. have prepared a fully conjugated structure by inserting a TTF moiety in the conjugated backbone.⁴ However, due to its insolubility, the obtained material could not be characterized. Yamamoto et al. reported a preparation of soluble π -conjugated polymers containing TTF units in the π -conjugated main chain.⁵ These polymers did not form CT complexes with an organic acceptor such as TCNQ, however.

The author has described the synthesis of new π -conjugated polymers having electron-donating dithiafulvene unit in the main chains by cycloaddition polymerizations of aldothioketenes derived from aromatic diyne monomers with their alkynethiol tautomers in Chapter 1.⁶ The UV-vis absorption spectra and cyclic voltammetry measurements showed an effective expansion of the π -conjugation system in the poly(dithiafulvene)s. In Chapter 2, the author reports the first π -conjugated polymer containing dithiafulvene units in the main chain formed CT complex with TCNQ. The resulting CT complex was soluble in common organic solvents.

Results and Discussion



Poly(dithiafulvene) (1) used in this study was prepared by the cycloaddition polymerization of the bis(aldothioketene) derived from 1,4-diethynylbenzene.⁶ In DMSO, 1 reacted with TCNQ to produce a dark green homogeneous solution. An excess amount of TCNQ against the repeating unit of 1 was added to a solution of 1 in DMSO, and the mixture was stirred for 15 min at room temperature. The polymer solution gradually turned to dark green, which indicated the charge-transfer (CT) complex formation. Due to very low solubility of TCNQ itself in DMSO at room temperature, unreacted TCNQ remained as a precipitate. After the precipitated TCNQ

was filtered off, the filtrate was evaporated to obtain a dark green powder. The resulting CT complex was soluble in acetonitrile, DMSO, DMF, acetone, and MeOH, partially soluble in THF, and not soluble in CHCl_3 , Et_2O , and H_2O . On the contrary, the starting polymer was soluble in DMSO and DMF, and partially soluble in acetone and methanol.

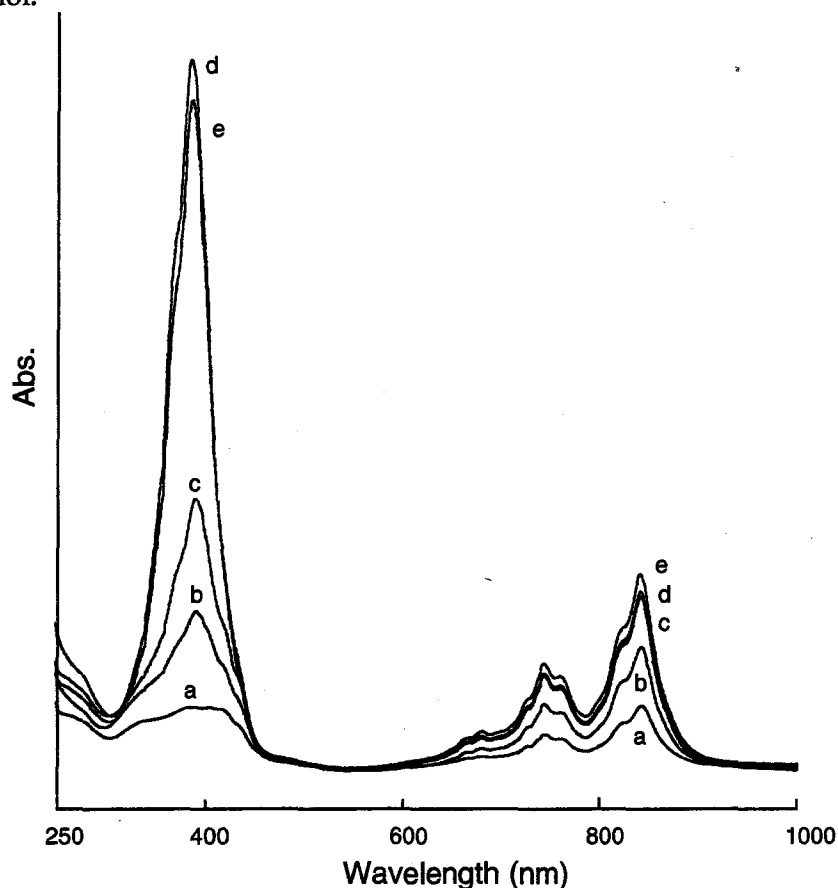


Figure 1. Dependence of the UV-vis absorption spectrum on the TCNQ feed ratio against the 1,3-dithiafulvene unit of **1**. $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0.1$ (a), 0.2 (b), 0.7 (c), 1.0 (d), and 1.5 (e).

The UV-vis absorption spectrum of the anion radical of TCNQ exhibits major maxima at 420 and 842 nm. The intensity ratio of the 420 and 842 nm band is about 0.5 for simple salts,⁷ and determination of this ratio serves as a useful criterion in characterization of TCNQ derivatives. TCNQ shows a strong absorption at around 395 nm. The UV-vis absorption spectrum of the CT complex of **1** with TCNQ showed absorption that was essentially a summation of the band characteristic of TCNQ and the anion-radical. The intensity ratio of the 395 and 842 nm band was approximately three. Figure 1 shows the dependence of the UV-vis absorption spectrum on the TCNQ feed ratio against the dithiafulvene unit of **1**. At $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0.1$, the absorption spectrum was a typical radical-anion salt of TCNQ. Increased feed ratio of TCNQ resulted in an increase in the absorption at 395 nm. The intensity at 842 nm was saturated below $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0.7$. In the relative intensity at 395 nm, the first saturation curve profile is observed below $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0.7$. Further increasing the feed ratio of TCNQ beyond $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0.7$.

1] = 1.0 did not increase the absorption at 395 nm, which clearly suggested a final formation of a complex containing about 1:1 ratio of dithiafulvene unit to TCNQ. These results indicate that the anion radical of TCNQ was initially formed by the charge-transfer reaction when TCNQ was added to the solution of **1**, and the remaining TCNQ was interacted with **2** as a partially charge-transferred form.

FT-IR spectrum of the sample containing about 1:1 ratio of dithiafulvene unit to TCNQ shows both frequencies corresponding to **1** and TCNQ (See Experimental Section). The degree of charge transfer can be determined by the frequency of the nitrile stretching band of TCNQ.⁸ Neutral TCNQ shows 2227 cm⁻¹ and fully ionic TCNQ is 2180 cm⁻¹. The spectrum of the CT complex of **1** with TCNQ shows a major band in C≡N stretching region at 2201 cm⁻¹ and a minor band at 2179 cm⁻¹ (Figure 2), indicating two different types of TCNQ molecules in the sample. The latter band was assignable to the anion radical of TCNQ. The major frequency at 2201 cm⁻¹ was shifted with respect to that of the partially charge-transferred TCNQ. The degree of charge transfer was estimated to be 0.62.^{8a} This value was almost same as those of most organic CT complexes.¹⁸ FT-IR spectrum of the sample containing about 3:1 ratio of dithiafulvene unit to TCNQ shows a major band in C≡N stretching region at 2177 cm⁻¹, indicating the anion radical of TCNQ was mainly formed. These observations are consistent with the UV-vis absorption analysis described above.

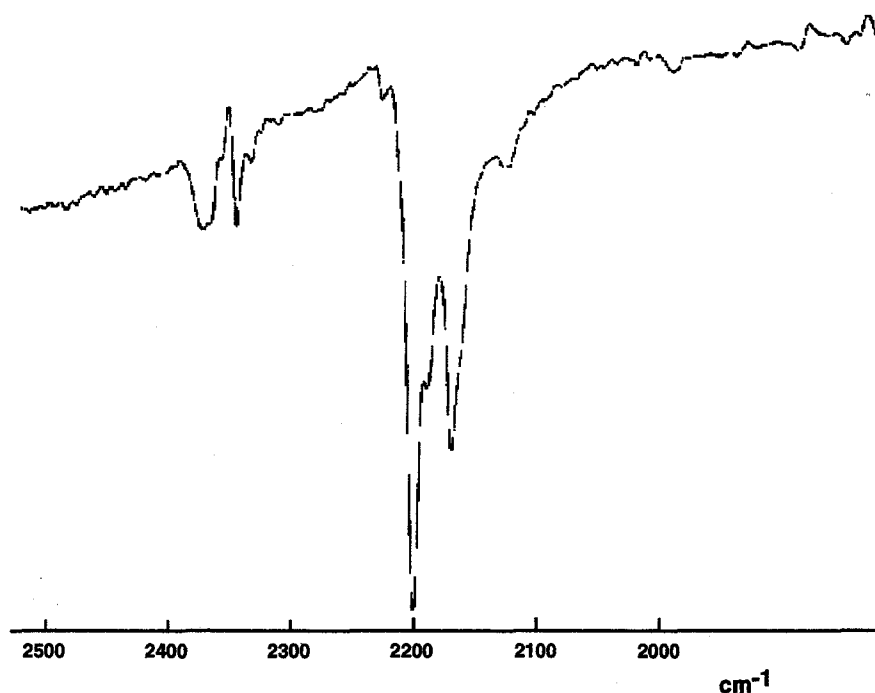


Figure 2. FT-IR spectrum of the CT complex of **1** containing about 1:1 ratio of dithiafulvene unit to TCNQ.

Figures 3 and 4 show the dependence of ¹H NMR spectrum on the TCNQ feed ratio against 2-benzylidene-4-phenyl-1,3-dithiole (**2**) as a model compound and the dithiafulvene unit of **1**. The ¹H NMR spectrum of the model compound **2** shows a peak for the benzylidene proton appeared at 6.7 ppm, along with multiplet peaks for the 1,3-dithiole ring proton at 7.2 ppm (Figure 3a). Although the benzylidene proton and the 1,3-dithiole ring proton of **2** disappeared after an excess amount of TCNQ was

added to the DMSO- d_6 solution of **2** (Figure 3c), the peaks at 6.7 and 7.2 ppm were still observed when a half equimolar amount of TCNQ was added to the DMSO- d_6 solution of **2** (Figure 3b). In addition to these peaks, several new peaks appeared between 6.8 and 7.2 ppm, indicating several different types of dithiafulvene molecules in the sample. In the ^1H NMR spectrum of the neutral poly(dithiafulvene) **1** (Figure 4a), a broad peak for the benzyldiene proton appeared at 6.7 ppm. The amount of TCNQ against the repeating unit of **1** to the DMSO- d_6 solution of **1** was increased, and benzyldiene proton at 6.7 ppm was shifted to a lower magnetic field (Figure 4b-d). Even 0.3 equimolar amount of TCNQ was added to the DMSO- d_6 solution of **1**, a broad peak appeared at 6.95 ppm and the peak for the neutral benzyldiene proton at 6.7 ppm was hardly observed (Figure 4c). These results indicated that electron density of the dithiafulvene units decreased by charge-transfer reaction with TCNQ and the positive charge in the dithiafulvene moieties was effectively delocalized in the π -conjugated polymer chain.

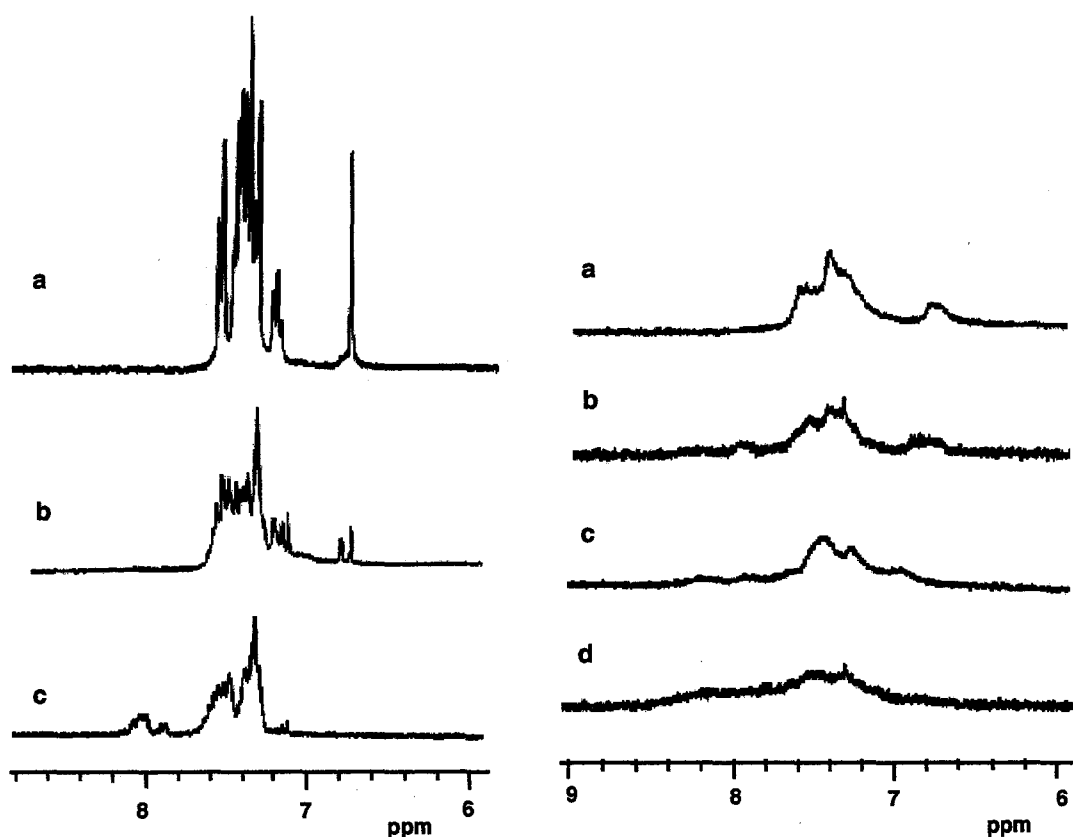


Figure 3 (left). Dependence of ^1H NMR spectrum on the TCNQ feed ratio against the dithiafulvene unit of **2** in DMSO- d_6 . $[\text{TCNQ}]/[\mathbf{2}] = 0$ (a), 0.5 (b), and 3 (c). **Figure 4** (right). Dependence of ^1H NMR spectrum on the TCNQ feed ratio against the model compound **1** in DMSO- d_6 $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{1}] = 0$ (a), 0.1 (b), 0.3 (c), and 3 (d).

The ^1H NMR spectrum of the neutral poly(dithiafulvene) **1** showed two broad peaks at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. Comparison of the intensities of the absorptions of the dithiafulvene protons in the repeating unit with those of the absorptions of the terminal thioamide protons resulted in the estimation of number-average degree of polymerization. The ^1H NMR spectrum after an excess

amount of TCNQ was added to the DMSO- d_6 solution of **1** showed very broad peak from 7.0 to 8.5 ppm assignable to aromatic and dithiafulvene protons of **1** and TCNQ, along with two broad peaks at 4.2 and 3.6 ppm attributed to the terminal thioamide protons. The peaks for unreacted TCNQ hardly appeared in the ^1H NMR spectrum due to the limited solubility of TCNQ in DMSO at room temperature. Comparison of the intensities of the absorptions of the aromatic region of **1** and TCNQ protons with those of the absorptions of the terminal thioamide protons showed a formation of a complex containing about 1:1 ratio of dithiafulvene unit to TCNQ.

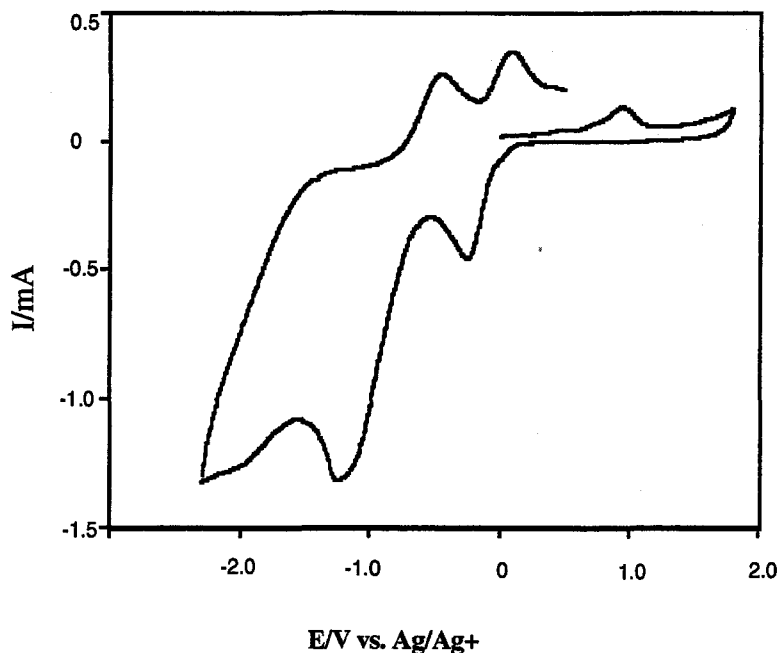


Figure 5. Cyclic voltammogram of the CT complex of **2** with TCNQ in an acetonitrile solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 300 mV/s.

To estimate the redox behavior of the CT complex of **1**, a cyclic voltammetric measurement was carried out (Figure 5). One oxidation peak was observed at 0.9 V vs Ag/Ag^+ , which can be assigned to one electron transfer from CT complex of **1** forming neutral TCNQ and the multi-cationic states of **1**. The oxidation peak corresponded to the neutral dithiafulvene unit was hardly recognized, i.e., cast film of **1** gave a single-broad oxidation peak at about 0.6 V vs. Ag/Ag^+ .^{6b} The two reduction peaks at about -0.3 and -1.0 V vs. Ag/Ag^+ , respectively were assignable to the reduction of neutral TCNQ.⁹ The drastic shift of the oxidation peak for the CT complex of **1** results from an electron withdrawing effect of TCNQ. The cyclic voltammetric analysis also confirmed that dithiafulvene unit in **1** was oxidized by TCNQ and neutral dithiafulvene moiety hardly existed.

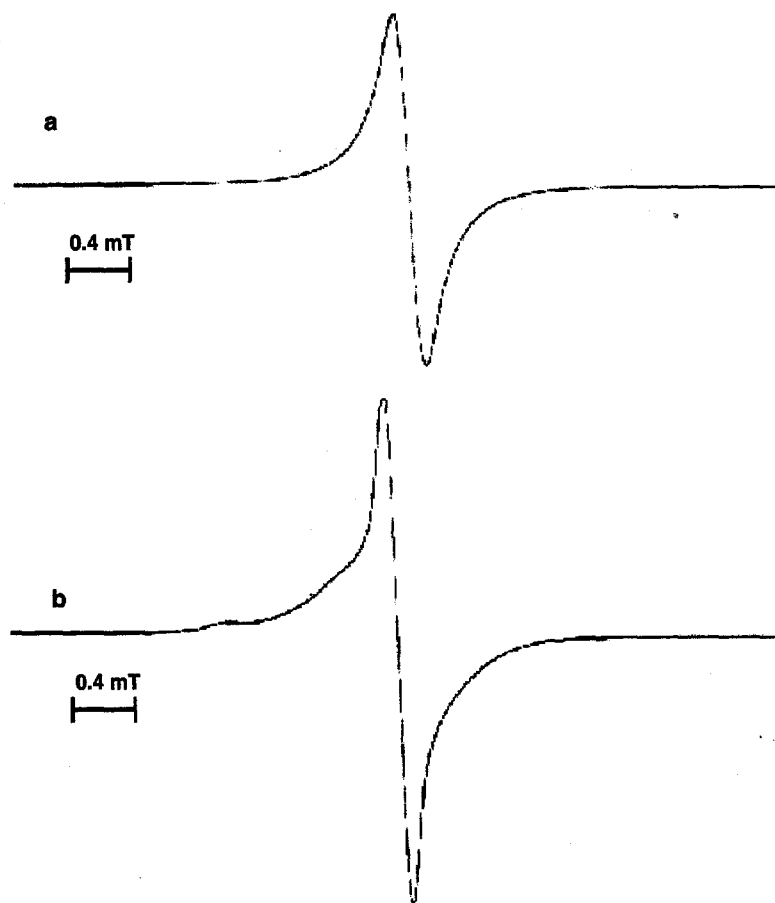


Figure 6. ESR spectra of the CT complex of **2** (a) and **1** (b). Both samples contained about 1:1 ratio of dithiafulvene unit to TCNQ.

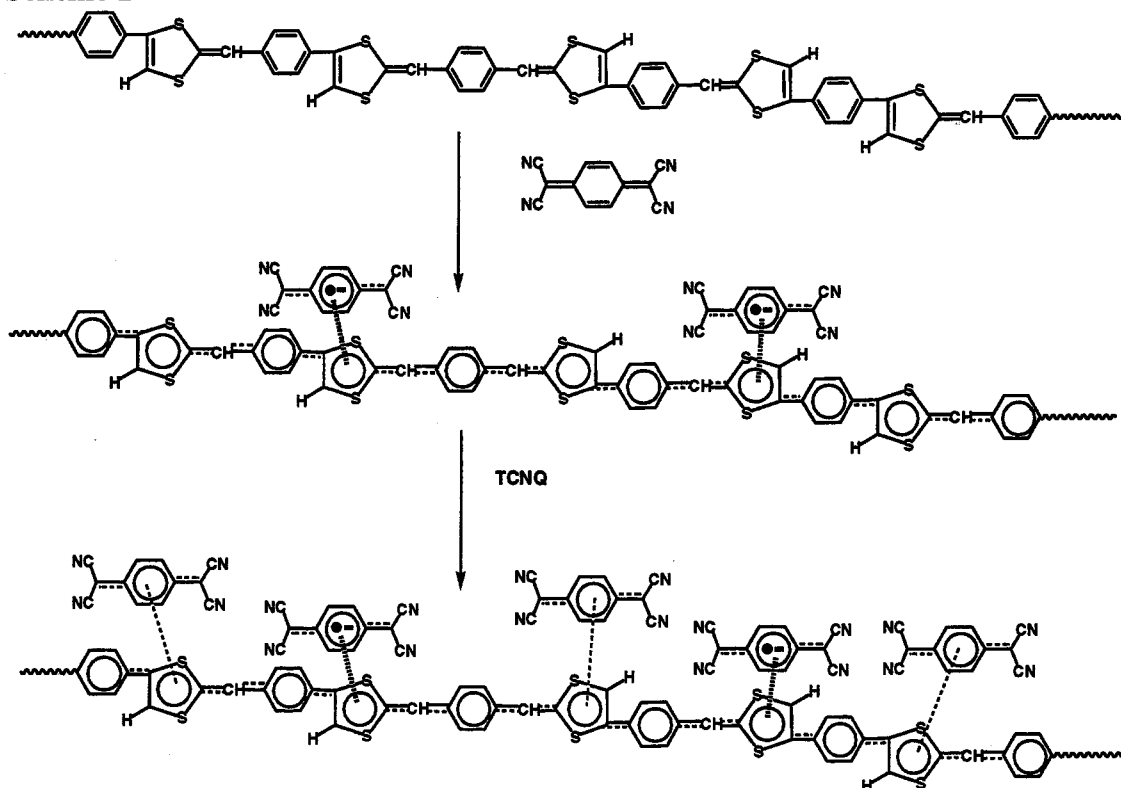
ESR spectra were measured for the isolated CT complexes of **1** and **2** diluted with KCl. The ESR spectrum of TCNQ reacting with **2** appeared a narrow singlet signal having g value of 2.003, indicating existence of a stable anion radical of TCNQ.¹⁰ The ESR spectrum of the CT complex of **1** consists of two types of signals. The g value and the lineshape of a sharp signal were completely same as those of the model CT complex. This sharp signal ($g = 2.003$) was assigned to the anion radical of TCNQ. One broad singlet line ($g = 2.013$) was clearly visible at higher modulation level. The g value of the broad signal is almost same as that of the ESR signal of TTF-TCNQ complex.¹¹ The broad signal may correspond to the partially charge-transferred TCNQ with **1**.

Before doping, **1** exhibits an electrical conductivity of $3 \times 10^{-7} \text{ S cm}^{-1}$ as measured on a cast film from 1,3-dimethyl-2-imidazolidinone. When **1** was dissolved in the same solvent with a slightly excess amount of TCNQ against dithiafulvene unit of **1**, a black CT complex was obtained. A cast film of the CT complex had a conductivity of $2 \times 10^{-4} \text{ S cm}^{-1}$, three orders of magnitude greater than that of the uncomplexed polymer. Oxidation of **1** with iodine instead of TCNQ increased the electrical conductivity to $1 \times 10^{-3} \text{ S cm}^{-1}$.

Summary

The author presents the first example of a soluble CT complex of π -conjugated polymers containing dithiafulvene units in the main chain with an organic acceptor such as TCNQ. The electronic absorption spectra suggested a formation of the CT complex containing about 1:1 ratio of dithiafulvene unit to TCNQ. The UV-vis absorption and FT-IR analyses indicated that the anion radical of TCNQ was initially formed by the charge-transfer reaction when TCNQ was added to the solution of **1**, and the remaining TCNQ was interacted with **1** as a partially charge-transferred form (Scheme 1). The charge-transfer reaction of dithiafulvene unit of the polymer was supported by the ^1H NMR and the cyclic voltammetric measurements. In the ^1H NMR spectra, the broad peak attributed to the benzyldiene proton of **1** was shifted to a lower magnetic field proportional to the TCNQ feed ratio against the dithiafulvene unit of **1**. This observation indicated that electron density of the dithiafulvene units decreased by charge-transfer reaction with TCNQ and the positive charge in the dithiafulvene moieties was effectively delocalized in the π -conjugated polymer chain. The oxidation level of the electron donating π -conjugated polymer can be controlled by the amount of the acceptor.

Scheme 1



Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Poly(dithiafulvene) (**1**) was prepared from 1,4-diethynylbenzene according to our previous report.^{13,14} The number-average molecular weight (M_n) of **1** used here was 3010 determined by ^1H NMR. Comparison of the intensities of the absorptions of the dithiafulvene protons in the

repeating unit with those of the absorptions of the terminal thioamide protons results in the estimation of number-average degree of polymerization. The model compound **1** was prepared according to ref. 15.

Measurements. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. For cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. The cyclic voltammogram of a cast film of **1** on an ITO electrode was measured in an acetonitrile solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 300 mV/s. ESR spectra were recorded at X-band frequency with a JEOL JES-RE spectrometer in quartz capillaries of 4 mm internal diameter. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit.

CT complex of **1 with TCNQ.** A typical experimental procedure is as follows. An excess amount of TCNQ (10 mg) against repeating unit of **1** was added to a solution of **1** (3 mg) in DMSO (0.5 mL), and the mixture was stirred for 15 min at room temperature. The solution was gradually turned to dark green. After the unreacted TCNQ was filtered off, the solvent was removed under the reduced pressure to obtain a dark green powder (yield: 5 mg). ^1H -NMR (δ , ppm): 1.2-1.7 (CH_2 of piperidine unit), 3.6 (N- CH_2 of piperidine unit), 4.2 (N- CH_2 of piperidine unit), 4.3 ($\text{CH}_2\text{C}(=\text{S})\text{N}<$), 7.2-8.2 (aromatic and dithiafulvene of **2** and TCNQ); IR (KBr, cm^{-1}) 2201 ($\text{C}\equiv\text{N}$ stretching of TCNQ), 2179 ($\text{C}\equiv\text{N}$ stretching of TCNQ), 1576 ($\text{C}=\text{C}$ vibration of the dithiafulvene unit), 1505 (terminal thioamide group).

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Chapter 3

Synthesis and Properties of π -Conjugated Poly(dithiafulvene)s by Cycloaddition Polymerization of Heteroaromatic Bisthioketenes

Abstract: π -Conjugated polymers (**2**) having electron-donating dithiafulvene units and typical heteroaromatic (thiophene or pyridine) units in the main chain were prepared by the cycloaddition polymerization of aldothioketenes derived from heteroaromatic diynes (2,5-diethynylthiophene, 2,5-diethynyl-3-hexylthiophene and 2,5-diethynylpyridine) with their alkynethiol tautomers. The obtained polymers were soluble in DMSO and DMF. The structures of the polymers were confirmed by ^1H NMR and IR spectra. The UV-vis absorption spectra of **2** suggested that the π -conjugation systems in the polymers expanded more effectively than the polymer obtained from 1,4-diethynylbenzene reported previously. The cyclic voltammetry analysis of **2a** (prepared from 2,5-diethynylthiophene) showed an anodic shift and a broadening of the oxidation peak for the dithiafulvene unit compared with that of 2,6-bis(2-thienyl)-1,4-dithiafulvene (**3**), due to the effective expansion of the π -conjugation in **2a**. All polymers **2** formed soluble charge-transfer complexes with TCNQ in DMSO. The UV-vis absorption and IR spectra of the resulting CT complexes indicated that different two types of TCNQ, anion radical of TCNQ and partially charge transferred TCNQ, interacted with the dithiafulvene unit in **2**. Undoped polymer **2c** (prepared from 2,5-diethynylpyridine) showed an unusual high electrical conductivity of $1.6 \times 10^{-4} \text{ S/cm}$ due to incorporation of the π -deficient pyridine unit in the dithiafulvene polymer. The CT complex of **2a** with TCNQ has a conductivity of $1.0 \times 10^{-4} \text{ S/cm}$, two orders of magnitude greater than that of the uncomplexed polymer **2a**.

Introduction

The chemistry of dithiafulvenes and their analogs, including tetrathiafulvalenes (TTF), has been the focus of a considerable interest because of their ability to form stable and highly conducting charge-transfer (CT) salts with a number of electron acceptors.¹ As scientists were fascinated by their unique electronic properties, there have been several attempts to incorporate such donor molecules into polymeric matrices in order to improve the processability of charge-transfer salts.² The design of dithiafulvene-based donors with linearly extended π -conjugation has progressively emerged as one of the main synthetic strategies towards higher dimensionality of the conduction process in the doped state.³ However, examples of polymers containing dithiafulvene derivatives in the π -conjugate main chain have been limited.⁴ In Chapters 1 and 2, the author described the synthesis of new π -conjugated polymers having dithiafulvene unit in the main chain by the cycloaddition polymerization of aldothioketenes derived from aromatic diynes with their alkynethiol tautomers.⁵ Although thioketenes are regarded as highly reactive and very useful species in organic reactions, similar to their ketene analogs,⁶ the direct use of thioketenes in polymer synthesis has been very limited. The UV-vis absorption spectra and cyclic voltammetry measurements showed an effective expansion of the π -conjugation system in the polymers. These polymers formed soluble CT complexes with tetracyanoquinodimethane (TCNQ).^{5a,c}

Dithiafulvene analogs including five-membered heterocyclic compounds such as furan, thiophene, and pyrrole have been reported.⁷ As the aromatic resonance energy of these five-membered heterocycles is lower than that of benzene, a better π -electron delocalization over whole donor molecule can be anticipated because of the fact such heterocyclic compounds forming quinonoid conformations easily in their π -conjugated system.

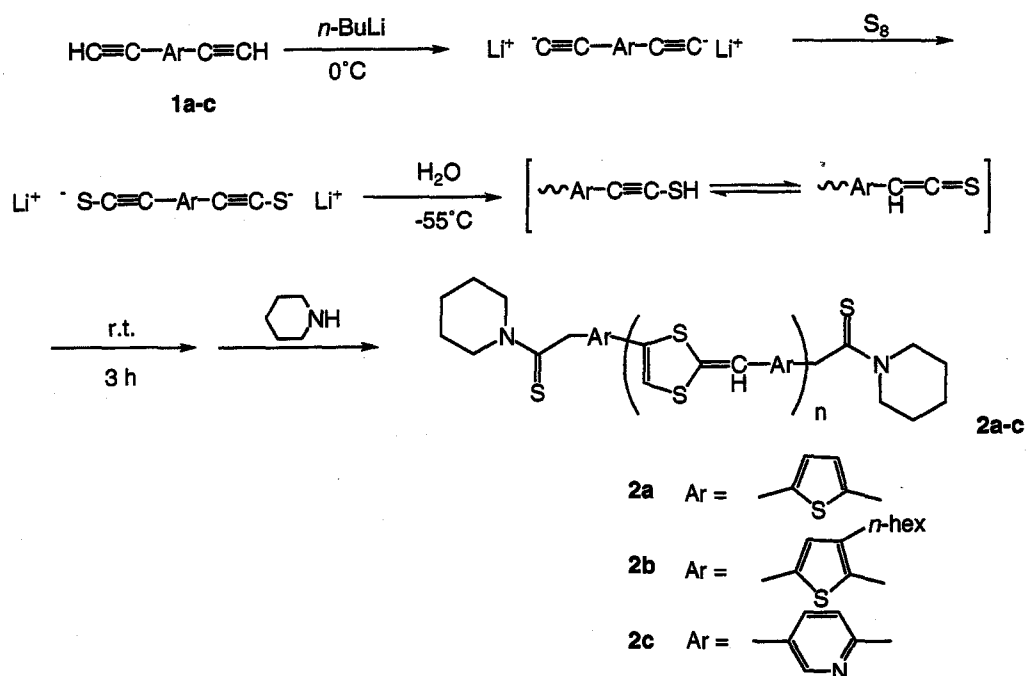
π -Conjugated polymers having donor-acceptor pairs in their backbone are fascinating materials in view of achieving a small band gap due to their intramolecular CT structures.⁸ Small band gaps for π -conjugated polymers are pursued because of their higher intrinsic (undoped) conductivity and they might give a clue for real intrinsically metallic organic polymer. Poly(pyridine)s are known as electron-accepting polymers and show n-doping property.⁹ Therefore, it is of interest to synthesize π -conjugated polymers comprising alternately-linked electron-donating dithiafulvene and pyridine moieties.

In this chapter, the author describes the synthesis and properties of new π -conjugated polymers having dithiafulvene and heteroaromatic units such as thiophene and pyridine in the main chain. CT complexes of those polymers with TCNQ are also studied.

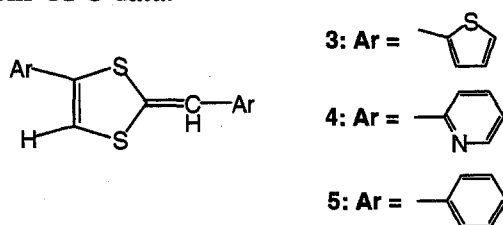
Results and Discussion

The polymerization reactions were carried out by the method of cycloaddition of aldothioketenes derived from heteroaromatic diynes **1** (Scheme 1). All polymers **2** were soluble in DMSO and DMF. Although one *n*-hexyl chain was attached on the thiophene unit, the solubility of **2b** was not improved. The molecular weight measurements were performed by GPC in eluent DMSO with poly(ethylene oxide) standard. The number-average molecular weight (M_n) of **2a** and **2c** were 3,230 and 4,170, respectively.

Scheme 1



The IR and ^1H NMR spectra of **2a-c** were reasonable for their structures compared with those of model compounds **3** and **4**^{6b,d} that were prepared from 2-ethynylthiophene and 2-ethynylpyridine, respectively. The IR spectra of **2a** and **2c** exhibited respective peaks at 1576 and 1584 cm^{-1} , corresponding to a C=C vibration of the dithiafulvene units. Those spectra also showed peaks at around 1500 and 1285 cm^{-1} which were assigned to the terminal thioamide moieties^{5a,b,6e,f} of the polymers. ^1H NMR spectrum of **3** showed peaks corresponding to dithiafulvene protons at 6.44 and 6.74 ppm in CDCl_3 . The peaks of the dithiafulvene protons shifted downfield to be detected at 6.97 and 7.16 ppm in $\text{DMSO}-d_6$. In the ^1H NMR spectrum of **2a** (Figure 1), a broad peak for the benzyldene proton of dithiafulvene appeared from 6.5 to 6.8 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.2 ppm in $\text{DMSO}-d_6$. This broadening was due to the relatively low solubility of **2a** in DMSO . The peaks for the terminal thioamide group were observed at 3.7, 4.1 and 4.4 ppm.^{5a,b,6e,f} The ^1H NMR spectrum of **2c** showed a broad peak from 6.5 to 7.0 ppm, assigned to the dithiafulvene protons and also showed peaks of the pyridyl protons at 7.4, 7.7-7.9 and 8.7 ppm. Comparison of the intensities of the absorptions of the dithiafulvene and the aromatic protons in the repeating unit with those of the absorptions of the terminal thioamide protons resulted in estimation of number-average degree of polymerization (DP) as 28 ($M_n = 5810$) in **2a**, 19 ($M_n = 5660$) in **2b** and 20 ($M_n = 4210$) in **2c**. These values are almost same as those from GPC data.



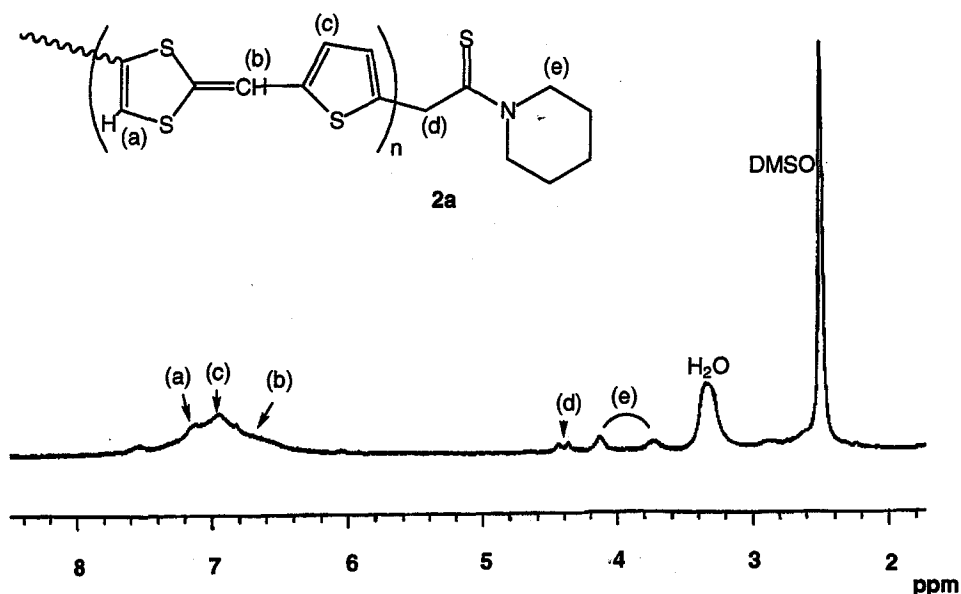


Figure 1. ^1H NMR spectrum of **2a** in $\text{DMSO}-d_6$.

Table 1. Synthesis of Dithiafulvene Polymers by Using Various Monomers

run	compound	yield (%)	M_n^a	UV λ_{max} (nm) ^b	oxidation potential (V) ^c
1	2a	65	5810	421	0.78
2	2b	25	5660	406 (sh) ^d	0.55
3	2c	72	4210	416 (sh) ^d	1.38
4	2d	76	5440	398	0.61
5	3	-		355	0.36
6	4	-		384	0.45

^a Determined from ^1H NMR. ^b Measured in a diluted CH_3CN solution at room temperature. ^c Measured in a CH_3CN solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 300 mV/s. ^d Shoulder peak of the spectra.

UV-vis absorption spectra of polymers and their model compounds were obtained for CH_3CN solutions. As shown in Figure 2, the UV-vis absorption spectra of the polymers **2a** and **2c** show largely bathochromic shift from those of their model compounds. The polymer **2a** showed an absorption in the visible range with a peak at 421 nm, due to the $\pi-\pi^*$ transition of the polymer. The peak position was largely shifted to longer wavelength by 66 nm from the absorption band of **3** (Figure 2 (a)). Moreover, UV-vis absorption of **2a-c** located at longer wavelength than that of the benzene analogue (**2d**) (Table 1, run 4), indicating that the π -conjugations through the heteroaromatic moieties are more effectively expanded than that through the benzene moiety. This fact, in thiophene polymers **2a** and **2b**, was caused by the lower aromatic resonance energy of the thiophene unit compared with that of the benzene ring. The lower energy absorption edge of **2c** was largely bathochromic shifted in comparison with that of the model compound **4**. The bathochromic shift of **4** from λ_{max} of **3** and that of 2-benzylidene-4-phenyl-1,3-dithiole (**5**) as benzene analogue ($\lambda_{\text{max}} = 352 \text{ nm}$)^{5a,b} suggested unique electronic state related to the donor-acceptor pair between the dithiafulvene unit and the pyridine unit. The smaller bathochromic shift of **2b** from

λ_{max} of **3**, compared with the bathochromic shift observed with **2a**, was due to a steric distortion of the side alkyl chain of the thiophene moiety.¹⁰

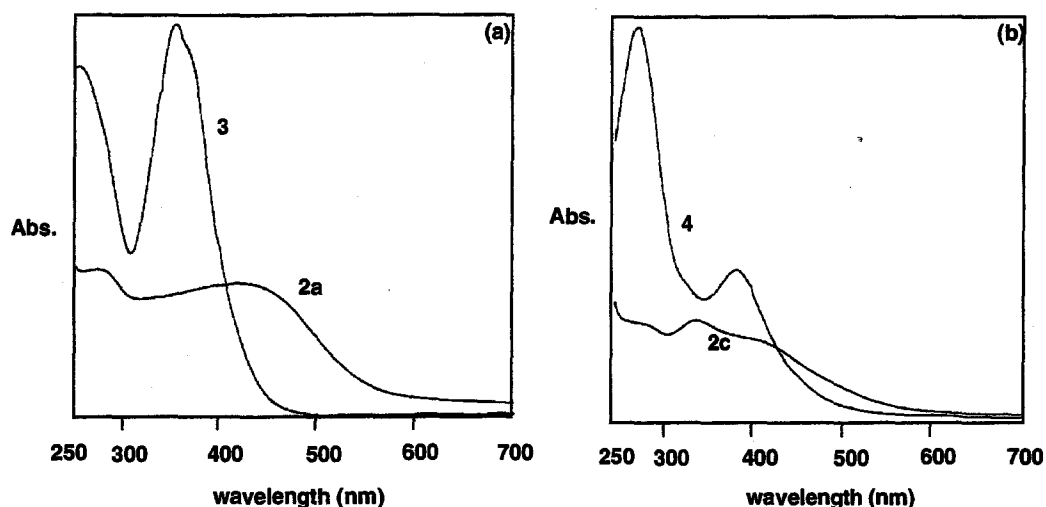


Figure 2. UV-vis absorption spectra of (a) **2a** and **3**, (b) **2c** and **4** in CH_3CN .

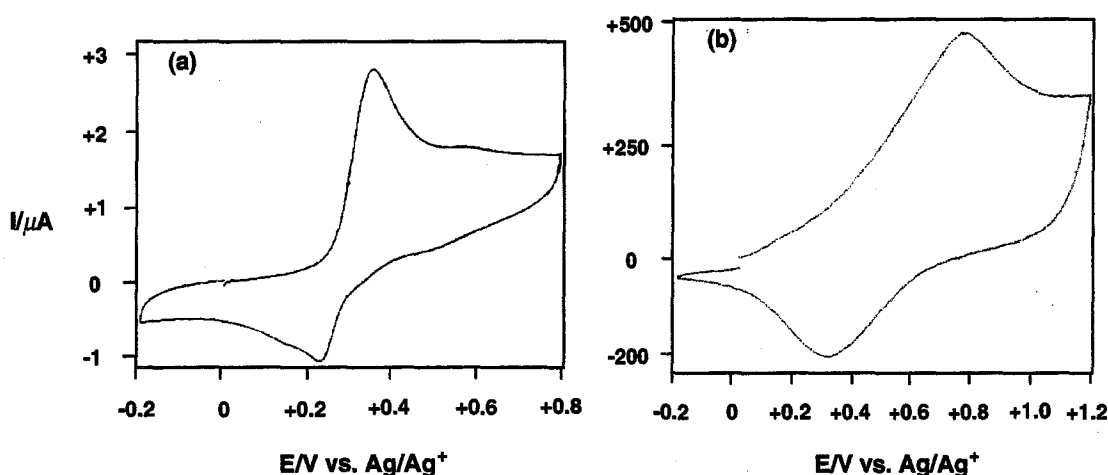


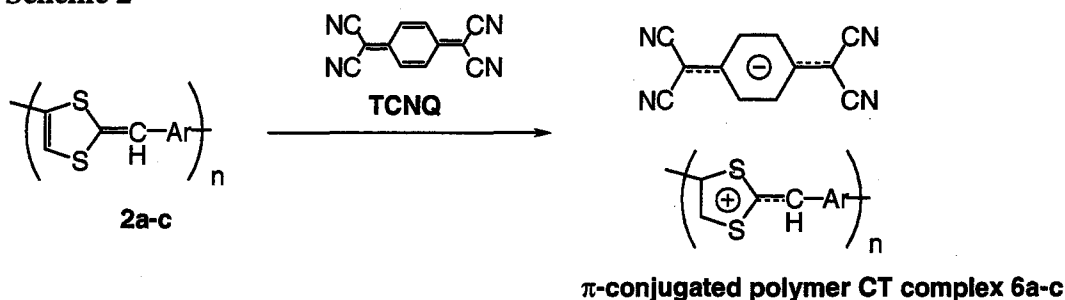
Figure 3. Cyclic voltammogram of (a) **3** (4×10^{-4} M; platinum working electrode) and (b) film of **2a** (thickness = $12\mu\text{m}$) on indium-tin-oxide (ITO) coated glass electrode, measured in CH_3CN solutions of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 300 mV/s.

The electrochemical redox behavior of the donors was studied by cyclic voltammetry. As shown in Figure 3, **3** showed a single oxidation peak at 0.36 V vs. Ag/Ag^+ . The value of the oxidation peak was less positive by 0.04 V than that of **5** ($E_{\text{pa}} = 0.40$ V),^{5b} indicating that the electron donating ability of **3** increased by the π -excessive thiophene moiety. The cast film of **2a** gave a single broad oxidation peak at 0.78 V and a reduction peak at 0.30 V vs. Ag/Ag^+ . The oxidation peak of **2a** was largely anodic shifted and broadened in comparison with that of **3**. Such an anodic shift and broadening of the peak have been reported for several electrochemically active π -conjugated polymers.^{9d,11} The fairly higher oxidation potential of **2a** compared with that of **2d** was also observed, whereas **3** shows the stronger electron donating property than its benzene analog. This result indicated that the dithiafulvene unit in **2a** caused a

higher stabilization against oxidation than that in **2d** due to the π -electron delocalization of **2a** was enhanced in comparison with that of **2d**.

The cast film of **2b** showed a lower oxidation peak than that of **2a**, suggesting that π -conjugation between dithiafulvene units through the thiophene having side alkyl chain was not so effective as that through the thiophene with no alkyl group. This behavior is consistent with the UV absorption analysis described above. Moreover, **2b** gave lower oxidation potential compared with the corresponding benzene polymer. The unusual high oxidation potential of the dithiafulvene unit of **2c** was caused by the effect of the π -deficient pyridine unit.

Scheme 2



The polymers **2a-c** formed complexes with TCNQ in DMSO (Scheme 2). To a solution of **2a-c** in DMSO, an excess amount of TCNQ against the repeating dithiafulvene unit of **2a-c** was added and the mixture was stirred for 15 min. TCNQ itself is hardly soluble in DMSO. After unreacted TCNQ was filtered off, the filtrates were evaporated to obtain dark green powders. The resulting CT complexes (**6a-c**) were soluble in common organic solvents such as DMSO, DMF, acetonitrile, acetone and methanol.

A degree of charge transfer can be determined by the frequency of the nitrile stretching band of TCNQ.¹² Neutral TCNQ shows at 2227 cm^{-1} and anion radical of TCNQ shows at 2180 cm^{-1} . IR spectra of **6a** showed two peaks in $\text{C}\equiv\text{N}$ stretching region at 2200 and 2180 cm^{-1} . This fact suggested that different two types of TCNQ interacted with polymer **2a**. The latter band was assignable to anion radical of TCNQ. The former peak was shifted by 27 cm^{-1} from neutral TCNQ, indicating the partially charge transferred TCNQ was in the complex. The degree of charge transfer was estimated to be 0.63 from the value of the peak difference.^{12a} IR spectra of **6b** and **6c** were similar to that of **6a**, both of which showed two $\text{C}\equiv\text{N}$ stretching bands of anion radical and partially charge transferred TCNQ (2197 cm^{-1} in **6b** and 2202 cm^{-1} in **6c**). The calculated values of degree of charge transfer in **6b** and **6c** were 0.68 and 0.59, respectively.^{12a} Degree of charge transfer of TCNQ in **6** has the following order, **6b**>**6a**>**6c**. This observation might be explained by the oxidation potential of polymer **2** determined from CV analysis. When formed complex with dithiafulvene polymers, TCNQ could accept much charge from the stronger donor (**6b**, $E_{\text{pa}} = 0.55$) and less charge from the weaker one (**6c**, $E_{\text{pa}} = 1.38$), resulting in the difference of degree of charge transfer.

UV-vis spectra of the CT complexes **6** in acetonitrile showed absorptions that were essentially a summation of the band characteristic of TCNQ and the anion radical. The appearances of the absorption bands between 650 and 900 nm were responsible for the anion radical of TCNQ.¹³ The strong peak at 390 nm were also observed in the

spectrum of **6**. Normal TCNQ shows an absorption at 395 nm. In the IR spectra of the polymer CT complexes **6**, the C≡N stretching bands due to neutral TCNQ could not be found so that the observed peaks at 390 nm in **6** should be corresponding to the partially charge transferred TCNQ.

In the ¹H NMR spectra of **6** in DMSO-*d*₆, comparison of the intensities of the absorption of the aromatic region and the dithiafulvene protons and the TCNQ protons with those of the terminal thioamide protons showed formations of both complexes containing about 1:1 ratio of dithiafulvene unit to TCNQ.^{5a,c}

The conductivities of the polymers were investigated at room temperature by conventional two-probe technique. Undoped **2a** and **2c** exhibited electrical conductivities of 1.2×10^{-6} S/cm and 1.6×10^{-4} S/cm, respectively. Extreme high intrinsic conductivity of **2c** was achieved in undoped state, due to an incorporation of a π -deficient pyridine unit in the dithiafulvene polymer. This unusual observation presumably resulted from the effective donor-acceptor pair of the dithiafulvene and the pyridine units. The CT complex **6a** had a conductivity of 1.0×10^{-4} S/cm, two orders of magnitude greater than that of the uncomplexed polymer **2a**, however **6c** showed 2.9×10^{-4} S/cm, not much improved compared with the undoped polymer.

Summary

We presented the synthesis and properties of the polymers with the electron donating dithiafulvene and the heteroaromatic units. The UV absorption analysis indicated that π -conjugation in **2a-c** was more effectively expanded than that in the phenyl analog polymer. The polymer **2** formed the CT complexes with TCNQ in DMSO. Different two types of TCNQ, anion radical of TCNQ and partially charge transferred TCNQ, interacted with the repeating dithiafulvene unit of the polymer, indicated by IR and UV spectra of **6**. The undoped **2c** showed unexpectedly high conductivity due to its donor-acceptor pair of the dithiafulvene and the pyridine units. The CT complexes **6** raised conductivities to exhibit the property as a semi-conductor.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N₂. 2,5-Diethynylthiophene,^{14a,b} 2,5-diethynyl-3-hexylthiophene^{14a,b,c} and 2,5-diethynylpyridine^{14a,b} were synthesized according to the literature.

Measurements. ¹H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography was carried out on TSK gel α -3000 by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. For cyclic voltammetry studies, thin polymer films (thickness, 10-20 μ m) were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in all CV measurements. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 source meter. The polymer film was prepared by dropping of a DMSO solution onto glass plates equipped with platinum electrodes, followed by drying in vacuo.

Polymerization. A typical experimental procedure is as follows. To a solution of 2,5-diethynylthiophene (132 mg, 1.00 mmol) in Et₂O (1.5 mL), 1.6 M solution of *n*-butyllithium in hexane (1.25 mL, 2.00 mmol) was added at 0 °C. After stirring for 0.5 h, the powder of sulfur (64 mg, 2.00 mmol) was added to the solution. The reaction mixture was stirred for 2 h, then cooled at -55 °C and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.3 mL) and stirred for 0.5 h. The mixture was then poured into a large quantity of Et₂O. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a dark brown-colored polymer was obtained.

2a. ¹H NMR (270 MHz, DMSO-*d*₆) δ 1.2-1.6 (CH₂ of piperidine unit), 3.7 (N-CH₂ of piperidine unit), 4.1 (N-CH₂ of piperidine unit), 4.4 (CH₂C(=S)N<), 6.5-6.8 (benzylidene proton), 7.0 (protons of thiophene), 7.2 (1,3-dithiole ring proton); IR (KBr, cm⁻¹) 2835, 1628, 1576, 1540, 1496, 1428, 1284, 1240. Anal. Calcd: C, 49.1; H, 2.4. Found: C, 48.3; H, 2.6.

2b. ¹H NMR (270 MHz, DMSO-*d*₆) δ 0.8 (-CH₂(CH₂)₄CH₃) 1.0-1.7 (-CH₂(CH₂)₄CH₃, and CH₂ of piperidine unit), 2.6 (-CH₂(CH₂)₄CH₃), (3.6 (N-CH₂ of piperidine unit), 4.2 (N-CH₂ of piperidine unit and CH₂C(=S)N<), 6.4-7.4 (thiophene and dithiafulvene protons); IR (KBr, cm⁻¹) 2918, 2848, 1626, 1575, 1550, 1504, 1454, 1292. Anal. Calcd: C, 60.4; H, 6.1. Found: C, 59.8; H, 6.0.

2c. ¹H NMR (270 MHz, DMSO-*d*₆) δ 1.2-1.6 (CH₂ of piperidine unit), 3.2 (N-CH₂ of piperidine unit), 4.3 (N-CH₂ of piperidine unit and CH₂C(=S)N<), 6.5-7.0 (dithiafulvene protons), 7.4 (pyridyl proton), 7.7-7.9 (pyridyl proton), 8.7 (pyridyl proton); IR (KBr, cm⁻¹) 1584, 1508, 1434, 1286, 1261. Anal. Calcd: C, 57.1; H, 3.1. Found: C, 57.3; H, 3.3.

Model Compounds. The model compounds **3** were prepared according to ref 6b, d.

2,6-Bis(2-thienyl)-1,4-dithiafulvene (3).^{6d} ¹H NMR (270 MHz, (CDCl₃) δ 6.44 (>C=CH-Ar, s, 1H), 6.74 (dithiole ring proton, s, 1H), 6.93-7.08 (thiophene, m, 4H), 7.24 (thiophene, m, 2H); IR (KBr) 1574, 1568, 1416 cm⁻¹.

2,6-Bis(2-pyridyl)-1,4-dithiafulvene (4).^{6d} ¹H NMR (270 MHz, (CDCl₃) δ 6.70-7.22 (dithiafulvene and pyridyl protons, m, 4H), 7.48 (pyridine, d, 1H), 7.50 (pyridine, d, 1H), 7.66 (pyridine, m, 2H), 8.59 (pyridine, q, 2H); IR (KBr) 1582, 1557, 1454 cm⁻¹.

CT Complexes of 2 with TCNQ. A typical experimental procedure is as follows. An excess amount of TCNQ against repeating unit of **2** was added to the solution of **2** in DMSO, and the mixture was stirred for 15 min. The solution gradually became dark green. After the unreacted TCNQ was filtered off, the solvent was evaporated to obtain a dark green powder.

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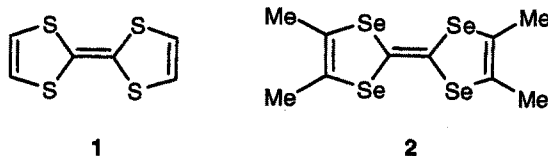
Chapter 4

π -Conjugated Poly(dithiafulvene)s and Poly(diselenafulvene)s: Effects of Side Alkyl Chains on Optical, Electrochemical and Conducting Properties

Abstract: Electron donating π -conjugated polymers with dithiafulvene moiety (4) or with diselenafulvene moiety (5) were prepared by cycloaddition polymerization of chalcogenoketenes derived from aromatic diynes (3). The solubilities of the polymers strongly depended on the structures. Since the large selenium atom increased interstack interaction between the units, the diselenafulvene polymers (5) showed lower solubilities than the corresponding dithiafulvene polymers (4). Attachment of long alkyl chains enhanced the solubilities in non-polar solvents. The structures of the polymers were confirmed by IR and ^1H NMR spectra. UV-vis measurements indicated that π -conjugations of the polymers were expanded; in particular, those of polymers containing the long alkyl side chains were unexpectedly developed. All the polymers showed electron-donating properties in cyclic voltammometry measurements and formed soluble charge-transfer complexes with TCNQ. After the complexation, the conductivities of the polymers raised efficiently.

Introduction

Dichalcogenafulvene derivatives have been widely used as electron donor components in the preparation of charge-transfer (CT) complexes and radical ion salts.¹ In the chemistry of the dichalcogenafulvenes, especially the focus has been centered on derivatives of tetrathiafulvalene (TTF, **1**). Since the discoveries of a high electrical conductivity in a chloride salt of TTF² and metallic behavior in the charge-transfer (CT) complex with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)³, there have been many studies of TTF-based materials that possess unusual electronic and magnetic properties.⁴ The recent developments in synthetic TTF chemistry have allowed the ready preparation of large quantities of derivatized TTFs, which are utilized not only for components of the molecular conductor but also π -rich redox active supramolecular systems.⁵ Meanwhile, replacement of sulfur by chalcogens with more diffuse orbitals (Se, Te) would enhance the interstack interaction to increase dimensionality of the conduction state. The resulting high dimensionality is considerably effective to improve the conducting performance of such organic metals at low temperature. For example, cation radicals of tetramethylselenafulvalene (TMTSF, **2**) have been reported to exhibit superconductivity below 5K due to the Se-Se interaction between the units.⁶



Hybridization between the dichalcogenafulvene derivatives and π -conjugated polymers is an attraction.^{7,8} The association of structural characters and properties may contribute to mutual fertilization by development of new materials of fundamental and technological interest. The conjugated polymers are basically low dimensional conductors, similarly to the dichalcogenafulvene-based CT salts. When intermolecular CT units between the dichalcogenafulvenes and π -acceptors are incorporated into conjugated polymers, electron mobility along the polymer backbone via π -conjugation, as well as along the stacking direction via π -orbital overlap would be improved (high dimension of conducting state).⁸ Furthermore, inter- and intramolecular Coulombic repulsions between the CT species would be suppressed to enhance the stacking CT formations due to the large number of sulfur atoms in the structure.⁸

A series of π -conjugated polymer with the dithiafulvene unit formed CT complexes with TCNQ.⁹ The polymer CT complexes showed highly improved electrical conductivities. In this chapter, the author reports on a successful and general synthesis of π -conjugated poly(dichalcogenafulvene)s by cycloaddition polymerizations of chalcogenoketenes. Comparisons of the poly(dithiafulvene)s with poly(diselenafulvene)s from various viewpoints are interesting. The author also demonstrates important effects of the polymer side chains on chemical and physical properties of the poly(dichalcogenafulvene)s.

Results and Discussion

The author employed three monomers (**3a-c**) with different side alkyl chains to prepare the poly(dichalcogenafulvene)s (**4**, **5**). Cycloaddition polymerizations of chalcogenoketenes and their alkynechalcogenol tautomer derived from **3** *in situ* successfully produced the poly(dithiafulvene)s **4** and the poly(diselenafulvene)s **5** (Scheme 1). End capping by piperidine to convert thioamides or selenoamides resulted in better solubilities of the obtained polymers than those of the polymers without end capping. Synthetic details of poly(dithiafulvene) **4a**

have been already reported in Chapter 1.^{9b} The report showed that molecular weights of the poly(dithiafulvene)s varied with the change of the reaction solvent and Et₂O was selected as the best reaction medium to achieve satisfactory degrees of the polymerization. In this work, Et₂O also acted as the most effective solvent to synthesize the poly(dithiafulvene)s **4b** and **4c**, however, the poly(diselenafulvene)s **5** were not obtained under the same condition. When THF was used instead of Et₂O, the polymerization toward **5** underwent smoothly.

Scheme 1

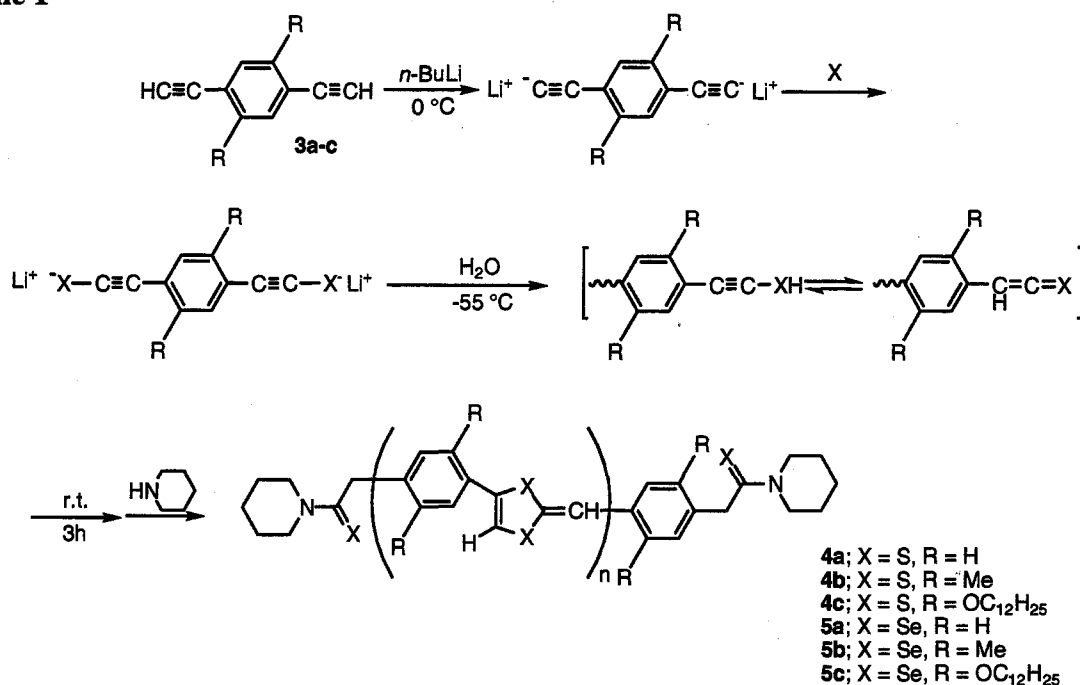


Table 1. Preparation of Poly(dichalcogenafulvene)s

entry	compound	yield (%)	solubility	molecular weight (<i>M_n</i>)
1	4a	76	DMSO, DMF	6810 ^a
2	4b	37	DMSO, DMF	3090 ^a
3	4c	68	CHCl ₃ , CH ₂ Cl ₂ , THF	8870 ^b
4	5a	95	Insoluble	-
5	5b	85	Partially soluble in DMSO	2110 ^{a,c}
6	5c	98	Partially soluble in CHCl ₃ , THF	5220 ^{b,d}

^a GPC was carried out by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol). ^b GPC were performed in chloroform at 25 °C by use of polystyrene standard samples. ^c DMSO soluble part. ^d Chloroform soluble part.

Solubilities of the polymers are summarized in Table 1. Similarly to **4a**, the poly(dithiafulvene) **4b** was soluble in aprotic polar solvents such as DMSO and DMF. Due to the substitution of the long alkyl chain, the polymer **4c** showed good solubility in CHCl₃, CH₂Cl₂ and THF, and was hardly soluble in DMSO and DMF. Solubilities of poly(diselenafulvene)s were found to be very limited, e.g. the polymer **5a** was completely insoluble in any solvent. The insolubility of **5a** prevented further investigations of the physical properties. In spite of the alkyl substitutions on the phenylene unit, the polymers **5b** and **5c** showed partial solubilities in organic solvents. These facts suggested that strong Se-Se interactions induced interunit stackings between the diselenafulvene moieties to give the low solubilities of **5**. 31 % of **5b**

was soluble in DMSO and the CHCl_3 soluble part of **5c** was 46 %. The polymers obtained in this chapter were subjected to gel permeation chromatography (GPC) measurement to determine molecular weights (Table 1). In case of the poly(diselenafulvene)s, the soluble parts of the polymers were examined.

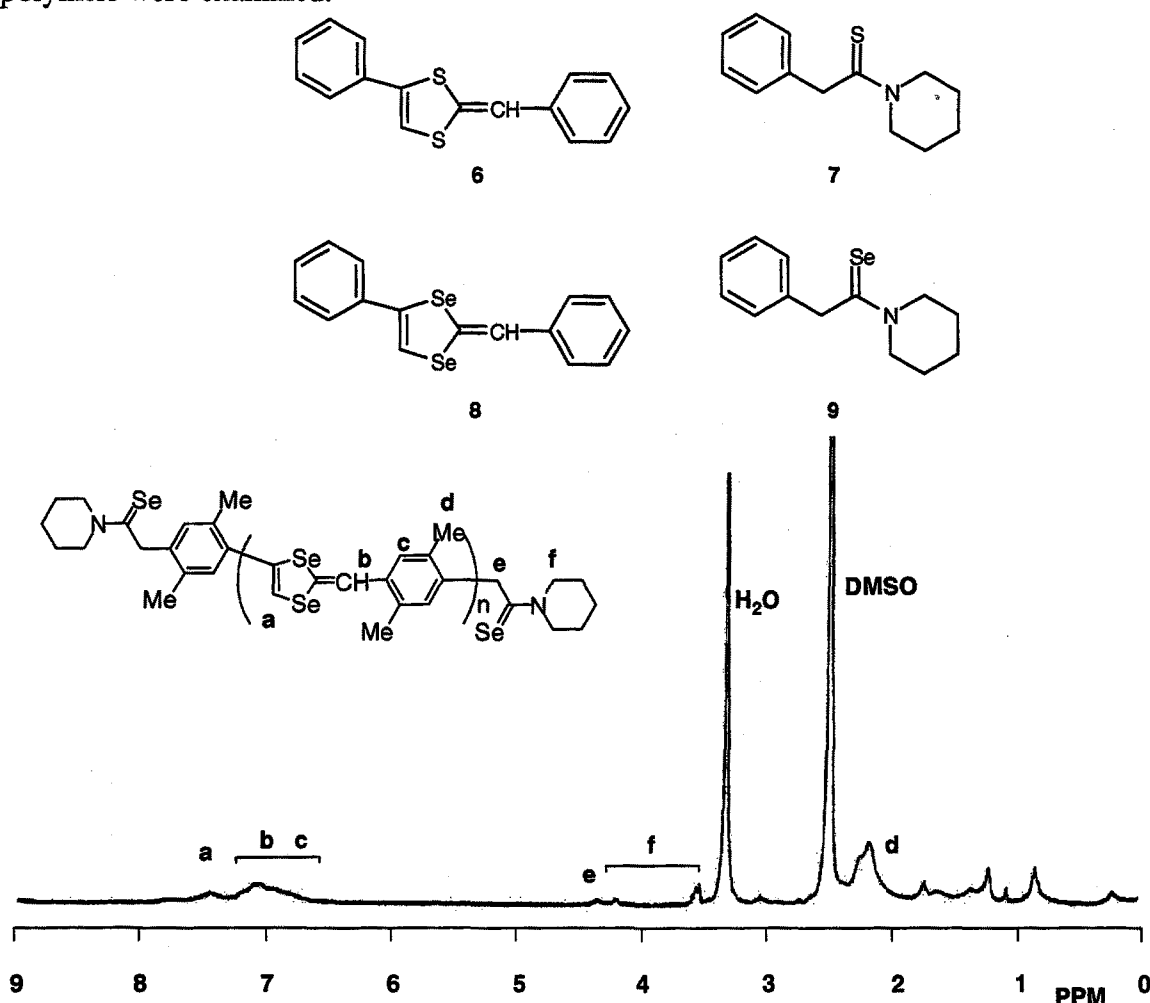


Figure 1. ^1H NMR spectrum of the soluble part of **5b** in $\text{DMSO}-d_6$.

The structures of the new poly(dithiafulvene)s (**4b**, **4c**) were clearly confirmed by IR and ^1H NMR spectroscopies compared with those of the model compounds which have been previously reported (**6**, **7**).^{9b} In order to support the structures of the poly(diselenafulvene)s, two model compounds (**8**, **9**) were synthesized. 2,6-Bisphenyl-1,4-diselenafulvene (**8**),¹⁰ that was obtained by the treatment of lithium 2-phenylethyneselenolate with water in THF, was used as a model compound for the diselenafulvene unit of **5**. An efficient reaction between phenylselenoketene and piperidine gave the model selenoamide (**9**)¹⁰ for the terminal unit of the poly(diselenafulvene)s. In the IR spectrum of **8**, peaks corresponding to the double bonds of the diselenafulvene moiety appeared at 1576 and 1558 cm^{-1} . The IR spectra of the soluble parts as well as insoluble parts of the poly(diselenafulvene)s **5** showed similar peaks between 1550 and 1580 cm^{-1} , suggesting that the structures of both parts of **5** are basically same and **5** contain the diselenafulvene moieties in the structures. The insoluble parts of **5** should consist of high molecular weight polymers. The ^1H NMR spectrum of the $\text{DMSO}-d_6$ soluble part of **5b** showed a broad peak corresponding to diselenole ring proton at 7.5 ppm and peaks for the terminal

selenoamide moiety at 3.6, 4.3 and 4.4 ppm. In the ^1H NMR spectrum of the CDCl_3 soluble part of **5c**, satisfactory peaks attributed to the diselenafulvene protons and the terminal selenoamide moiety were observed.

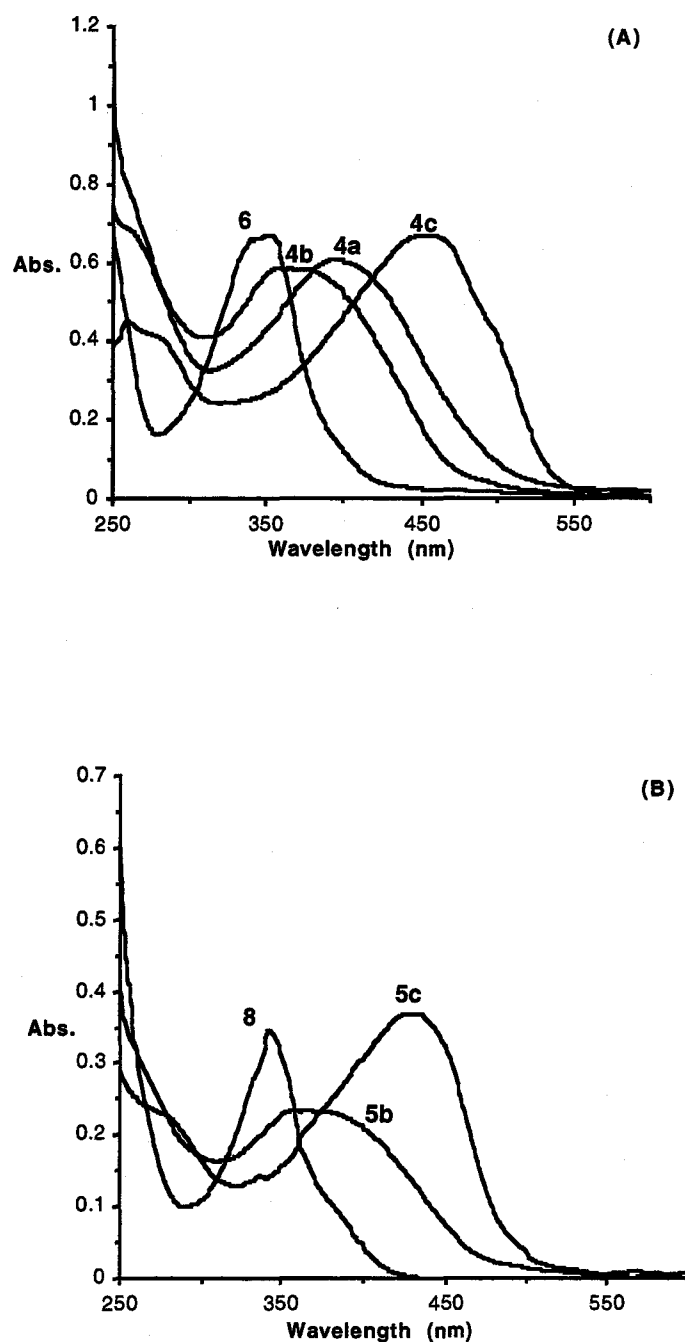


Figure 2. UV-vis absorption spectra of (A) **4a** and **4b** in CH_3CN , **4c** and **6** in CHCl_3 , (B) the soluble part of **5b** in CH_3CN , the soluble part of **5c** and **8** in CHCl_3 .

UV-vis absorption study of the polymers in the solution was performed (Figure 2, Table 2). The peaks due to π - π^* transitions of **4** and the soluble parts of **5** were located at longer wavelengths than those of the corresponding model compounds, indicating efficient π -electron delocalizations in the polymer systems. In the series of the poly(dithiafulvene)s, methyl substitution on benzene ring gave rise to blue shift from the absorption of **4a** due to a steric distortion of **4b** in CH_3CN . UV-vis measurement of **4c** showed a notable feature of the conjugation. In spite of substitutions of large alkoxy units, the π -conjugation system of **4c** in CHCl_3 was the most effectively expanded. This fact suggests that a bulky alkoxy chain increased the π -conjugative effect of **4c**. Each soluble part of the poly(diselenafulvene) (**5b** in CH_3CN , **5c** in CHCl_3) had an absorption with a similar peak position to its analogous poly(dithiafulvene). The π -conjugation system of **5c** was also highly developed by the alkoxy chain. Photoelectron spectroscopy, X-ray and UV-vis studies have shown that regio-regular polythiophenes with long side chains are more planer and stacked in the structures and polythiophenes with short side chains are more helical in nature.¹¹ It appears that such an enhanced coplanarity by long side chains affords the effective π -conjugations of **4c** and **5c**. Aggregations of the side chains occurred in **4c** and **5c** might cooperatively give the conjugative effects.^{11d}

Table 2. Physical Properties of Poly(dichalcogenafulvene)s

entry	compound	UV λ_{max} (nm)	oxidation peak (V) ^c	conductivity ^d (non-doped, S/cm)	conductivity ^d (TCNQ complex, S/cm)
1	4a	398 ^a	0.60	3×10^{-7}	2×10^{-4}
2	4b	366 ^a	0.55	8×10^{-7}	9×10^{-4}
3	4c	451 ^b	0.74	$<10^{-7}$	4×10^{-6}
4	5b	377 ^a	0.59	2×10^{-6}	2×10^{-4}
5	5c	429 ^b	0.79	1×10^{-7}	4×10^{-6}
6	6	358 ^b	0.40	-	-
7	8	341 ^b	0.44	-	-

^a UV spectra were measured in CH_3CN . ^b UV spectra were measured in CHCl_3 . ^c Cyclic voltammograms were obtained in CH_3CN solution containing 0.1 M $[\text{NEt}_4]\text{BF}_4$. Scan rates were 300 mV/s. ^d Electrical conductivities were measured at room temperature by two-probe technique.

The electrochemical redox behaviors of the donors were studied by cyclic voltammetry (CV) (Table 2). The model compounds **6** and **8** showed single oxidation peaks at 0.40 and 0.44 V vs Ag/Ag^+ , respectively. The value of the oxidation peak for the dithiafulvene **6** was less positive by 0.04 V than that of **8**, indicating that the electron donating ability of **6** is slightly stronger than that of **8**. The cast films of the polymers (**4** and **5**) were also electroactive and gave irreversible broad oxidation peaks between 0.5 and 0.8 V vs Ag/Ag^+ . UV-vis and CV measurements suggested that the oxidation potential and the π -electron delocalizations of the polymers are correlative. The oxidation potentials of the polymers shifted anodically with the development of the π -conjugations. The oxidation potentials as well as the conjugation systems can be finely tuned by the attachment of substituents on the benzene ring in the systems of the poly(dichalcogenafulvene)s.

The poly(dichalcogenafulvene)s formed CT complexes with TCNQ. After adding an excess amount of TCNQ to a polymer solution, it gradually turned to be dark green. The unreacted TCNQ was filtered off, and then the filtrate was evaporated to obtain a dark green powder as a polymer CT complex. The resulting complexes derived from **4a**, **4b** and **5b** were soluble in acetonitrile, DMSO, DMF, acetone, and MeOH. The CT complexes composed of **4c** or **5c** were soluble in THF, CHCl_3 , and CH_2Cl_2 . The UV-vis absorptions of the polymer CT complexes exhibited λ_{max} at 845, 762 and 745 nm, which were responsible for the anion-radical of TCNQ.¹² The conductivities of the polymers were measured at room temperature by two-probe technique and are summarized in Table 2. After complexation with TCNQ, the conductivities of the polymers increased remarkably. In case of **4a** and **4b**, the values were raised approximately 1000 times higher than those of the uncomplexed polymers. The relatively low conductivities of **4c** and **5c** complexes suggested incomplete complexations with TCNQ in the solid states because of the steric hindrances of the long alkoxy groups.

Summary

The author presented here the synthesis and properties of the π -conjugated polymers with the electron donating dichalcogenafulvene units. The low solubilities of the poly(diselenafulvene)s in organic solvents resulted from the large Se-Se interunit interaction. UV absorption analysis indicated that π -conjugations in **4** and **5** were efficiently developed. In particular, the most effective π -conjugations were unexpectedly achieved in the systems of the polymers attaching the long alkyl side chains. The polymers acted as good electron donors, similarly to the low molecular weight model compounds. In these polymer systems, the changes of substituents on the benzene ring can easily lead to the tuning of the oxidation potentials. The polymers formed the semiconducting CT complexes with TCNQ. Some polymers showed highly improved conductivities (three orders of magnitude greater than those of the uncomplexed polymers) after the complexations.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2 . 1,4-Diethynyl-2,5-dimethylbenzene (**3b**)¹³ and 1,4-diethynyl-2,5-bis(dodecyloxy)benzene (**3c**)¹⁴ were synthesized according to the literatures. Syntheses of the dithiafulvene **6** and the thioamide **7** have been described in a previous paper.^{9b}

Measurements. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. GPC measurements of **4b** and **5b** were carried out on TSK gel a-3000 by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. GPC of **4c** and **5c** were performed with a Shodex K-803 in chloroform at 25 °C by use of polystyrene as standard samples. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer in CH_3CN solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurements. For the CV of the polymers, thin polymer films were prepared on indium-tin-oxide (ITO) coated glass electrodes by casting from their solutions. The electrodes were dried under vacuum. For the CV of the model compounds, they were dissolved in the CH_3CN solution containing the supporting electrolyte. Platinum working electrode was used, instead of ITO. Electrical conductivities were measured at room temperature by two-probe technique using a Keithley 2400 source meter. The polymer films were prepared by dropping of

the polymer solutions onto glass plates equipped with platinum electrodes, followed by drying *in vacuo*.

Polymerization. A typical procedure is as follows. To a solution of a diethynyl compound (0.50 mmol) in a solvent (Et₂O or THF, 4.0 ml), 1.6 M solution of n-butyllithium in hexane (0.65 ml, 1.04 mmol) was added at 0 °C. The reaction mixture was kept at 0 °C for 0.5 h and powder of sulfur or selenium (1.00 mmol) was added. After stirring the mixture for 2 h at 0 °C, water (18 mg) was carefully added at -55 °C. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. The mixture was then poured into a large quantity of Et₂O or hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, the polymeric compound was obtained.

4b. Yield: 37 %. ¹H NMR (DMSO-*d*₆, ppm): δ 1.2-1.6 (CH₂ of piperidine unit), 2.3 (-CH₃ on phenyl moiety), 3.6 (N-CH₂ of piperidine unit), 4.2 (N-CH₂ of piperidine unit and -CH₂C(=S)N<), 6.7 (benzylidene and aromatic protons), 7.2 (aromatic and 1,3-dithiole ring protons); IR (KBr, cm⁻¹) 1576, 1550, 1290, 1262.

4c. Yield: 68 %. ¹H NMR (CDCl₃, ppm): δ 0.9 (-OC₁₁H₂₂-CH₃), 1.1-1.6 (-OC₂H₄-C₉H₁₈-CH₃ and CH₂ of piperidine unit), 1.8 (-OCH₂-CH₂-C₁₀H₂₁), 3.8-4.2 (-OCH₂-C₁₁H₂₃ and N-CH₂ of piperidine unit), 4.3 (N-CH₂ of piperidine unit and -CH₂C(=S)N<), 6.8 (benzylidene and aromatic protons), 7.0-7.2 (aromatic and 1,3-dithiole ring protons); IR (KBr, cm⁻¹) 1580, 1288, 1262.

5a. Yield: 95 %. IR (KBr, cm⁻¹) 1575, 1556.

5b. Yield: 85 %. ¹H NMR (DMSO-*d*₆ soluble part, ppm): δ 1.2-1.5 (CH₂ of piperidine unit), 2.2 (-CH₃ on phenyl moiety), 3.6 (N-CH₂ of piperidine unit), 4.3 (N-CH₂ of piperidine unit), 4.4 (-CH₂C(=S)N<), 6.7-7.4 (benzylidene and aromatic protons), 7.5 (1,3-diselenole ring proton); IR (KBr, cm⁻¹) 1576, 1553, 1292.

5c. Yield: 68 %. ¹H NMR (CDCl₃, ppm): δ 0.9 (-OC₁₁H₂₂-CH₃), 1.1-1.5 (-OC₂H₄-C₉H₁₈-CH₃ and CH₂ of piperidine unit), 1.8 (-OCH₂-CH₂-C₁₀H₂₁), 3.8-4.1 (-OCH₂-C₁₁H₂₃ and N-CH₂ of piperidine unit), 4.2 (N-CH₂ of piperidine unit and -CH₂C(=S)N<), 6.9 (aromatic protons), 7.1 (benzylidene proton), 7.5 (1,3-diselenole ring protons); IR (KBr, cm⁻¹) 1577, 1555, 1291.

Model Reactions

2,6-Bisphenyl-1,4-diselenafulvene (8).¹⁰ 1.6 M solution of n-butyllithium in hexane (0.65 ml, 1.04 mmol) was added to a stirred solution of phenylacetylene (102 mg, 1 mmol) in THF (2 ml), cooled at 0 °C. When the addition was completed, the reaction mixture was stirred at 0 °C for 0.5 h and powder of selenium (79 mg, 1.00 mmol) was added. After stirring the mixture for an additional 2 h at 0 °C, water (1 ml) was carefully added at -78 °C. The temperature of the mixture was allowed to rise at room temperature and the two layers were separated. The organic solution was dried with MgSO₄ and the solvent was removed, yielding a diselenafulvene (146 mg, 81 %). IR (NaCl): 1576, 1558 cm⁻¹. ¹H NMR (270 MHz, DMSO-*d*₆): δ 7.23-7.48 (m, 11H), 7.85 (s, 1H).

1-(2-Phenyl-1-selenoxoethyl)-piperidine (9).¹⁰ To a solution of piperidine (2.5 ml, 25 mmol) in Et₂O (1 ml) was added 1.6 M solution in hexane of n-butyllithium (1.56 ml, 2.50 mmol) at -30 °C. Phenylacetylene (255 mg, 2.50 mmol) was added to the reaction mixture. The temperature of the mixture was allowed to rise to 80 °C. The powder of selenium (197 mg, 2.5 mmol) was added, and the mixture was stirred for 2 h, and then 1N HCl (5 ml) was added. The brown organic layer was separated, and the aqueous phase was extracted with Et₂O. The combined organic phase was dried over anhydrous MgSO₄, and evaporated to give the product (604 mg, 91 %). ¹H NMR (CDCl₃) δ 1.28 (m, 2H), 1.73 (m, 4H), 3.55 (t, 2H), 4.39 (t, 2H), 4.52 (s, 2H), 7.35 (m, 5H).

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Chapter 5

Synthesis and Properties of Oxygen, Methylene and Alkylene Bridged Poly(dithiafulvene)s

Abstract: Polymerization by cycloaddition between aldothioketene and its alkynethiol tautomer (derived *in situ* from a diyne) leading to the formation of dithiafulvene unit linked polymers has been studied. Two aromatic diynes (bis(4-ethynyldiphenyl)methane (**1a**) and 4,4'-diethynyldiphenyl ether) (**1b**) were used as starting materials with the aim of obtaining non π -conjugated methylene and oxygen bridged aromatic poly(dithiafulvene)s. The poly(dithiafulvene) derived from bis(4-ethynyldiphenyl)methane can be considered as an interesting precursor to a small band gap polymer having alternating aromatic and quinonoid moieties. Further, two aliphatic diynes (1,7-octadiyne (**3a**) and 1,9-decadiyne (**3b**)) were also subjected to cycloaddition polymerization in order to obtain aliphatic poly(dithiafulvene)s containing localized electron rich dithiafulvene units. The polymers obtained were characterized by IR, ^1H NMR, GPC and cyclic voltammetry. The electron donating property of the polymers was evident from charge transfer (CT) complex formation with an electron acceptor 7,7,8,8-teracyanoquinodimethane (TCNQ). The CT complexes were characterized by IR, ^1H NMR, and UV-vis spectroscopy.

Introduction

Recently, a lot of research has been directed toward the synthesis of tetrathiafulvalene (TTF) unit containing polymers,¹ due to the unusual solid state properties of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) charge transfer (CT) salts.² A dithiafulvene (DTF) structure also shows a strong electron donating property³ due to an aromatic stability and ease of formation of the resultant 1,3-dithiolium ion. The 1,3-dithiolium ion is an unsaturated five membered ring cation in which each sulfur can contribute a pair of 3 p electrons. However, reports of polymers containing the DTF unit are relatively few. Mulvaney et al. have reported polymerization of vinyl carboalkoxy dithiole derivatives⁴ and polycondensation of dihydroxy substituted dithiafulvene monomers to form polyesters, polyurethanes and polyhydrazides containing the dithiafulvene ring.⁵ In Chapter 1, the author has reported the synthesis and characterization of new π -conjugated polymers containing the dithiafulvene unit in the main chain by cycloaddition polymerization of aldothioketenes derived from π -conjugated diynes.⁷ The UV-vis absorption spectra and cyclic voltammetry measurements showed an effective expansion of the π -conjugation system in the polymers. The π -conjugated poly(dithiafulvene)s formed soluble CT complexes with TCNQ. The CT complexes with the π -conjugated polymers are a new class of conducting materials.

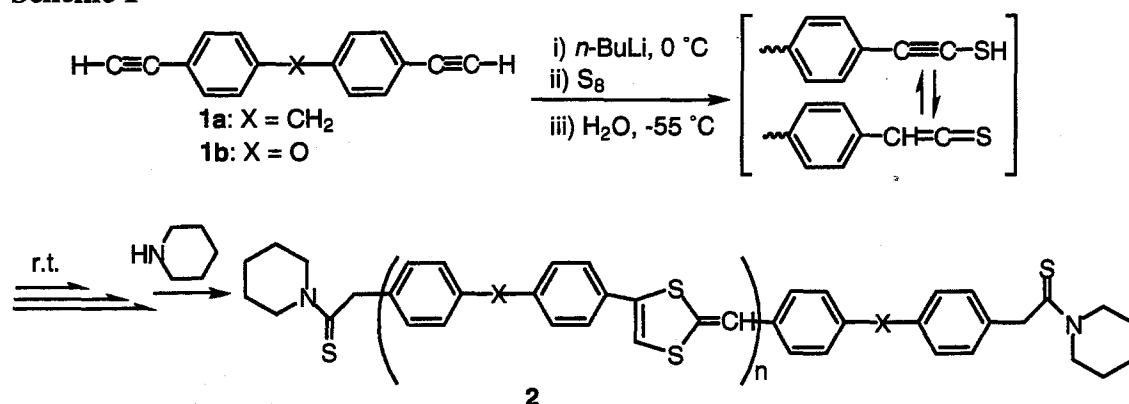
In the present chapter, non π -conjugated oxygen, methylene and alkylene bridged poly(dithiafulvene)s are synthesized as shown in Scheme 1. The oxygen and the methylene bridged aromatic poly(dithiafulvene)s were prepared starting from aromatic diynes containing a methylene or an ether link, bis(4-ethynyldiphenyl)methane (**1a**) and 4,4'-diethynyldiphenyl ether (**1b**), respectively. It was aimed to compare the properties of these polymers with the fully aromatic π -conjugated poly(dithiafulvene)s⁶ and to study the effect of the methylene and the ether linkage.

Another reason for an interest of the author is that the methylene linked aromatic poly(dithiafulvene) may serve as a precursor polymer to an alternating aromatic and quinonoid moiety containing small band gap conducting polymer. It has been reported⁷ that sp^3 -carbon bridged heteroaromatic polymers serve as precursors to small band gap conducting or semi-conducting polymers based on poly(heteroarylene methine)s.⁸ The precursor methylene polymers were subjected to oxidative dehydrogenation using 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) leading to alternating aromatic and quinonoid moieties in the main chains.⁹ The lowering of band gap was attributed to the introduction of the alternating quinonoid moieties in the polymer chains.

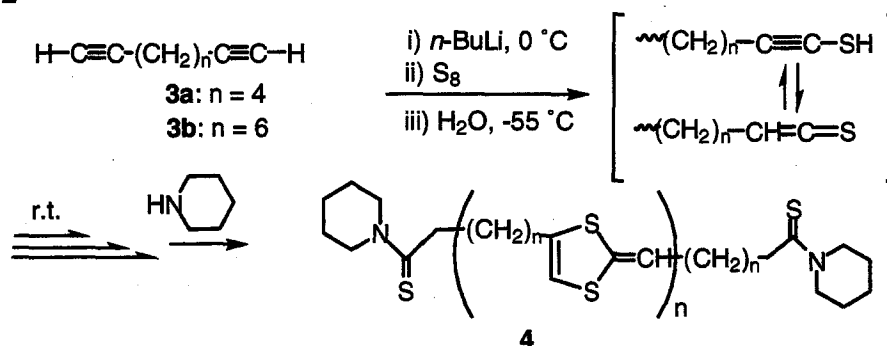
In addition to the methylene and the ether linked aromatic diynes, two aliphatic diynes, 1,7-octadiyne (**3a**) and 1,9-decadiyne (**3b**), were also used as starting materials in order to obtain aliphatic poly(dithiafulvene)s containing localized dithiafulvene units (Scheme 2). All the polymers obtained were characterized by IR, ¹H NMR, GPC and cyclic voltammetry. Charge transfer complexes of the polymers were prepared with TCNQ and the CT complexes were characterized by IR, ¹H NMR, and UV-vis spectroscopy.

Results and Discussion

Scheme 1



Scheme 2



Poly(dithiafulvene)s were synthesized by the cycloaddition polymerization as shown in Schemes 1 and 2. Treatment of the diynes with *n*-butyllithium followed by sulfur formed lithium thioalkynolates. The alkynethiols were formed by treatment with water as a proton source. The alkynethiols underwent cycloaddition with their aldothioketene tautomers resulting in the formation of the dithiafulvene unit that builds the polymeric chains. Piperidine was used for an end-capping, since it reacts with an aldothioketene to form a thioamide as the terminal end group.

Table 1. Results of Cycloaddition Polymerization of Aldothioketenes Derived from Various Diynes

entry	monomer	solvent	yield (%)	M_n^a	M_n^b	M_w^b
1	1a	THF	28	4370	1770	3240
2	1a	Et ₂ O	50	4370	1800	2270
3	1b	THF	39	4960	1980	3280
4	1b	Et ₂ O	53	4100	1750	2290
5	3a	THF	32	1700	1090	15200
6	3a	THF	40	1950	1050	20450

^a Determined from ¹H NMR. ^b Determined by GPC (DMSO) and poly(ethylene glycol) standards.

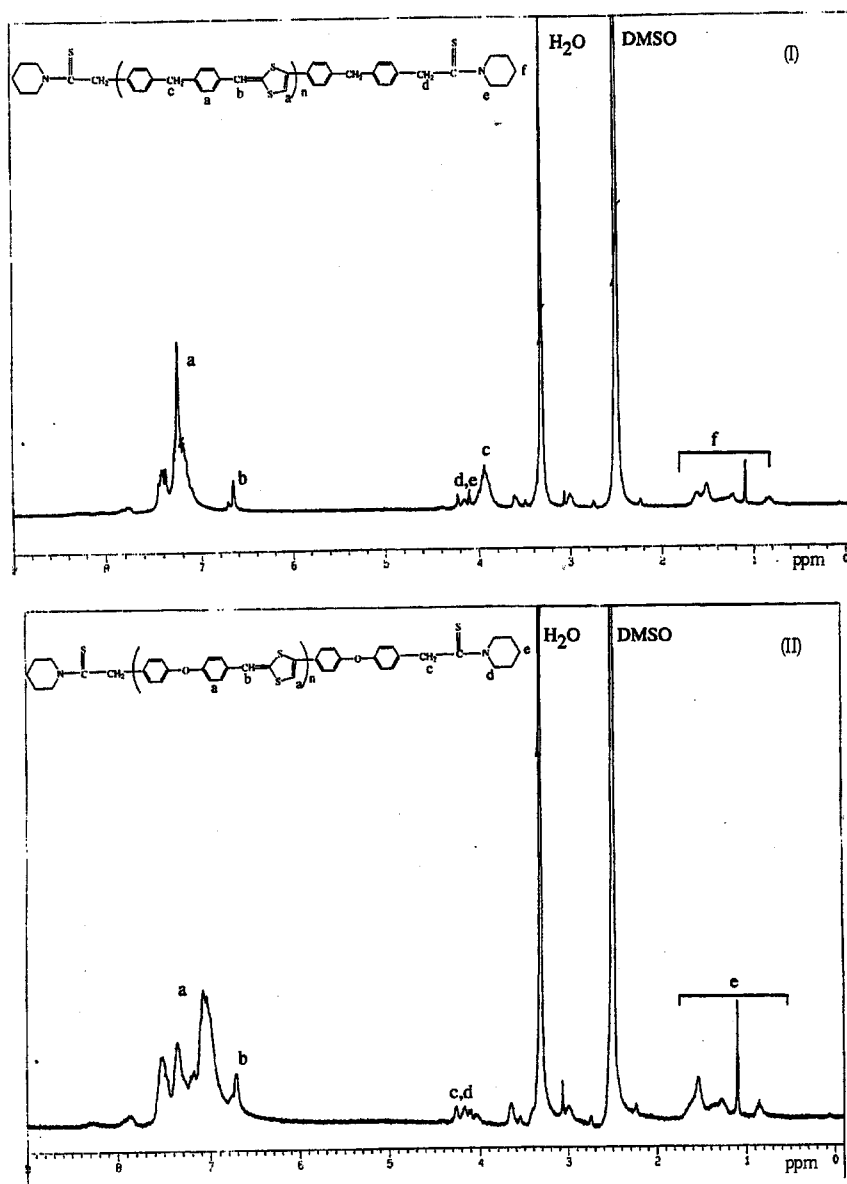


Figure 1. ^1H NMR of (I) **2a** and (II) **2b** in $\text{DMSO}-d_6$

Results of cycloaddition polymerization of bis(4-ethynyldiphenyl)methane (**1a**) and 4,4'-diethynyldiphenyl ether (**1b**) are summarized in Table 1 (entries 1-4). The polymers (**2a** and **2b**) were soluble in DMSO and partially soluble in THF, acetone and methanol. The structures of **2a** and **2b** were confirmed by IR and ^1H NMR spectroscopies compared with those of the model compounds, i.e., 2-benzylidene-4-phenyl-1,3-dithiole and 1-(2-phenyl-1-thioxoethyl)-piperidine⁶. The ^1H NMR of **2a** showed the benzylidene proton at 6.65 ppm and at 6.71 ppm in the case of **2b**, well separated from the aromatic and dithiafulvene ring protons (Figure 1). Polymerization using Et_2O as a solvent increased the yields of the polymers. Based on the integration of the benzylidene proton and the terminal thioamide protons, the number average molecular weights of **2a** (entry 2) and **2b** (entry 4) were calculated as 4370 and 4100,

respectively. GPC analysis gave values of $M_n = 1800$ and $M_w = 2270$ for **2a** (entry 2) and $M_n = 1750$ and $M_w = 2290$ for **2b** (entry 4) with respect to poly(ethylene glycol) standards. The values of the molecular weights obtained from ^1H NMR can be considered to be more accurate than that from GPC. The relatively low molecular weights of the polymers might be due to the solubility limits in the solvents for polymerization.

The results of the cycloaddition polymerization starting from the aliphatic diynes 1,7-octadiyne (**3a**) and 1,9-decadiyne (**3b**) in THF are also shown in Table 1 (entries 5-6). The products obtained were partially soluble in THF, acetone and methanol and soluble in hot DMSO. In the ^1H NMR of the products (Figure 2), the dithiole and the alkene protons of the dithiafulvene moiety were clearly observed at 6.18 ppm and 5.35 ppm, respectively. Based on the value of the integration of the peak at 4.18 ppm attributed to the N-CH_2 of the terminal thioamide¹⁰ and that at 6.18 ppm (dithiole ring proton), the number-average molecular weights of **4a** and **4b** were calculated to be 1700 and 1950, respectively. The integration of the aliphatic protons (2.4 to 1.0 ppm) was, however, observed to be 2.7 times greater than that expected for a polymer having a pure poly(dithiafulvene) structure.

Both GPC traces of **4a** and **4b** showed broad multimodal molecular weight distributions with high molecular weight polymers ($M_n = 15400$) in addition to low molecular weight products ($M_n = 3400$ and 1300). A small amount of DMSO was added to **4a** and stirred for 24 h at room temperature. An insoluble fraction (46 wt%) was collected and dissolved in hot DMSO and subjected to GPC measurement. The GPC trace of this fraction showed predominantly the high molecular weight polymers ($M_n = 15400$). The ^1H NMR spectrum of this fraction showed absence of the dithiafulvene protons, implying that the structure of the high molecular weight fraction was other than a poly(dithiafulvene) structure. In order to understand the formation of the two types of products, a model reaction was carried out using 1-octyne as a starting material¹¹. The product obtained was analyzed by ^1H NMR, IR, ^{13}C NMR and GPC. A thin layer chromatographic analysis of the product showed formation of two types of products. After separation by a column chromatography, a major product was obtained in 70 % yield. The major product was subjected to GPC measurement using CHCl_3 as an eluent. The number-average molecular weight and the molecular weight distribution of the product was 1500 and 1.36, respectively. The ^1H NMR of the major product showed signals only in aliphatic regions. The minor product was an expected cycloaddition product by ^1H NMR analysis. These results indicated that in addition to the expected cycloaddition reaction leading to the dimer, side reactions such as homopolymerization type reactions of the $>\text{C}=\text{C}<$ and $>\text{C}=\text{S}<$ of the thioketene intermediate have resulted in the formation of the oligomeric product. Thioketenes are known to be highly reactive species¹² and a possibility exists of an anionic polymerization as in polymerization of ketenes.¹³ In contrast, a model reaction of phenylacetylene gave a quantitative yield of an expected 2-benzylidene-4-phenyl-1,3-dithiole.⁶

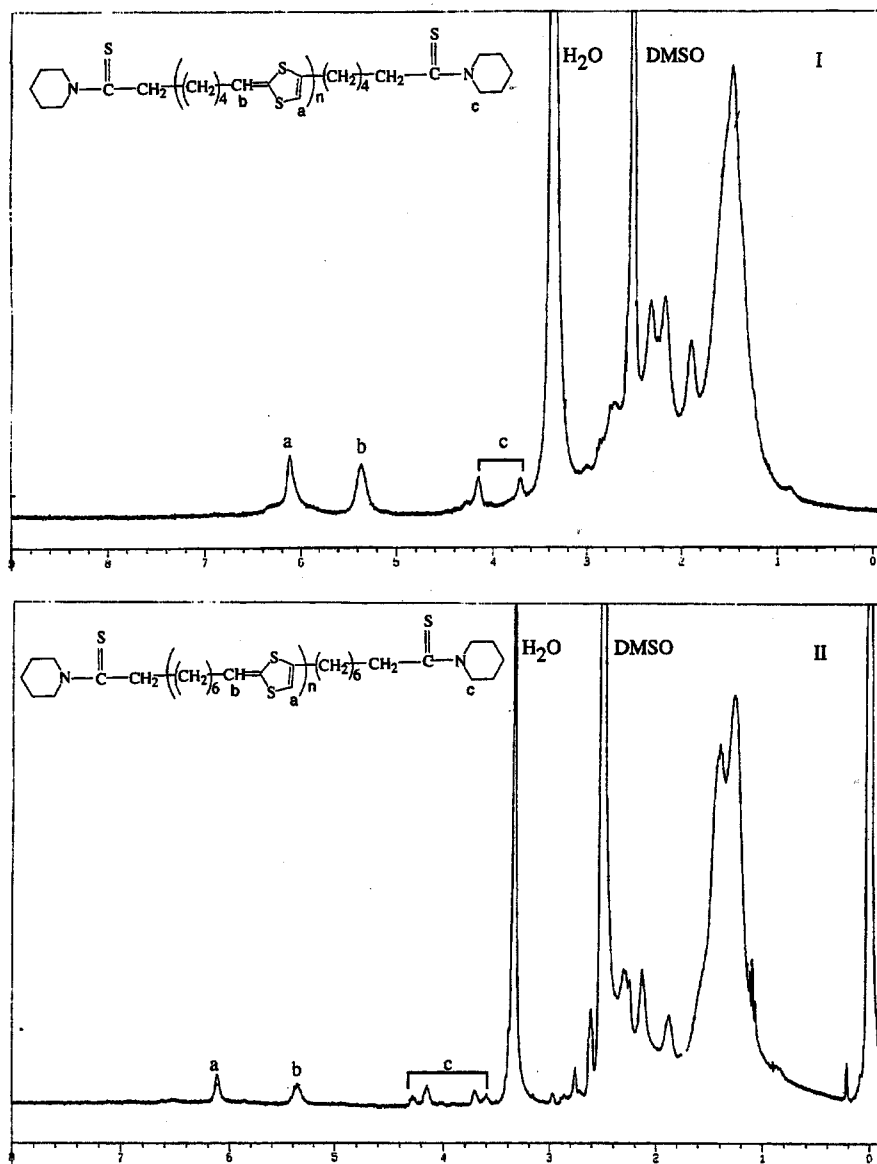


Figure 2. ^1H NMR of (I) **4a** and (II) **4b** in $\text{DMSO}-d_6$

A similar type of competing reactions with the diynes as starting materials can explain the formation of the high molecular weight polymers derived from an anionic homopolymerization of thioketene moieties to form some cross-linking structures. The low molecular weight products were expected polymers containing DTF unit. Assuming a polythioketone structure for the high molecular weight fraction and based on the integration of the ^1H NMR spectrum, the product obtained appears to consist of 45% of the expected poly(dithiafulvene) and 55 % of the polythioketone side product. Integration of the gel permeation chromatogram of **4a** gave a value of 54 % for the expected poly(dithiafulvene) ($M_n = 3400$ and 1300) and 46 % for the high molecular weight side product ($M_n = 15400$). When Et_2O was used as a solvent for the

polymerization, the ^1H NMR of the obtained product did not show any signals in the 5 to 6 ppm range.

The yields of the expected dithiafulvene structure in the model reaction of 1-octyne and the desired poly(dithiafulvene)s in the polymerization of the aliphatic diynes were lower compared with used the quantitative yield in the model reaction of phenylacetylene⁶ and the higher yields of poly(dithiafulvene) obtained starting from aromatic diynes. These results suggest that an aromatic thioketene ($\text{Ph-C}=\text{C}=\text{S}$) favors the cycloaddition reaction to form the dithiafulvene unit.

In the UV-vis absorption spectra of diluted acetonitrile solutions of **2a** and **2b**, the peak due to the π - π^* transition of the polymer appeared at 356 nm. This value was the same as that of the model compound, 2-benzylidene-4-phenyl-1,3-dithiole.⁶ In the case of the π -conjugated poly(dithiafulvene) derived from 1,4-diethynylbenzene, this peak was bathochromic shifted to $\lambda_{\text{max}} = 398 \text{ nm}$.⁶

The polymers **2a** and **2b** were also characterized by cyclic voltammetry. In an anodic scan, irreversible oxidation peaks due to an oxidation of dithiafulvene units were observed at 0.60 V vs. Ag/Ag^+ in the case of **2a** and at 0.48 V vs. Ag/Ag^+ in the case of **2b** at a scan rate of 300 mV/s. The lower oxidation potential of **2b** may be attributed to the ease of formation and higher stability of the corresponding 1,3-dithiolium ion due to extended resonance stabilization by participation of the lone pair of electrons on oxygen in **2b**. In the cathodic scan, a reversible wave was observed which might be attributed to a new redox system formed as a result of oxidative dimerization of the dithiafulvene units.^{6b} In the literature, oxidative dimerization of dithiafulvenes has been known to form tetrathiafulvalenes (TTF) vinylogues.¹⁴ The polymer **4a** was found to be electrochemically active and showed a broad oxidation peak at 1.3 V.

In order to elucidate the electron donating properties of the polymers, they were reacted with an electron acceptor like TCNQ. All the polymers studied formed charge-transfer (CT) complexes with TCNQ that were soluble in acetonitrile, THF and DMSO. The CT complexes were characterized by IR, ^1H NMR, and UV-vis spectroscopy.

In the case of the CT complexes of the aromatic poly(dithiafulvene)s with TCNQ, ^1H NMR spectra were recorded as a function of [repeating unit of the polymer]/[TCNQ] (Figure 3). The ^1H NMR spectrum of **2a** without TCNQ showed peaks at 6.65 ppm (benzylidene proton) and 7.1 to 7.5 ppm (aromatic and dithiafulvene ring proton). When the feed ratio of TCNQ was 0.3, intensity of the peak at 6.65 ppm decreased. On further addition of TCNQ (ratio 0.6) the intensity of the peak at 6.65 ppm decreased further and a new peak at 7.01 ppm was also observed. The new peak at 7.01 ppm is assumed to arise from the charge transferred dithiolium ion structure. On further increase in the TCNQ (ratio 0.9) the peak at 6.65 ppm disappeared completely and peaks were observed only at 7.01 ppm and from 7.18 to 7.86 ppm.

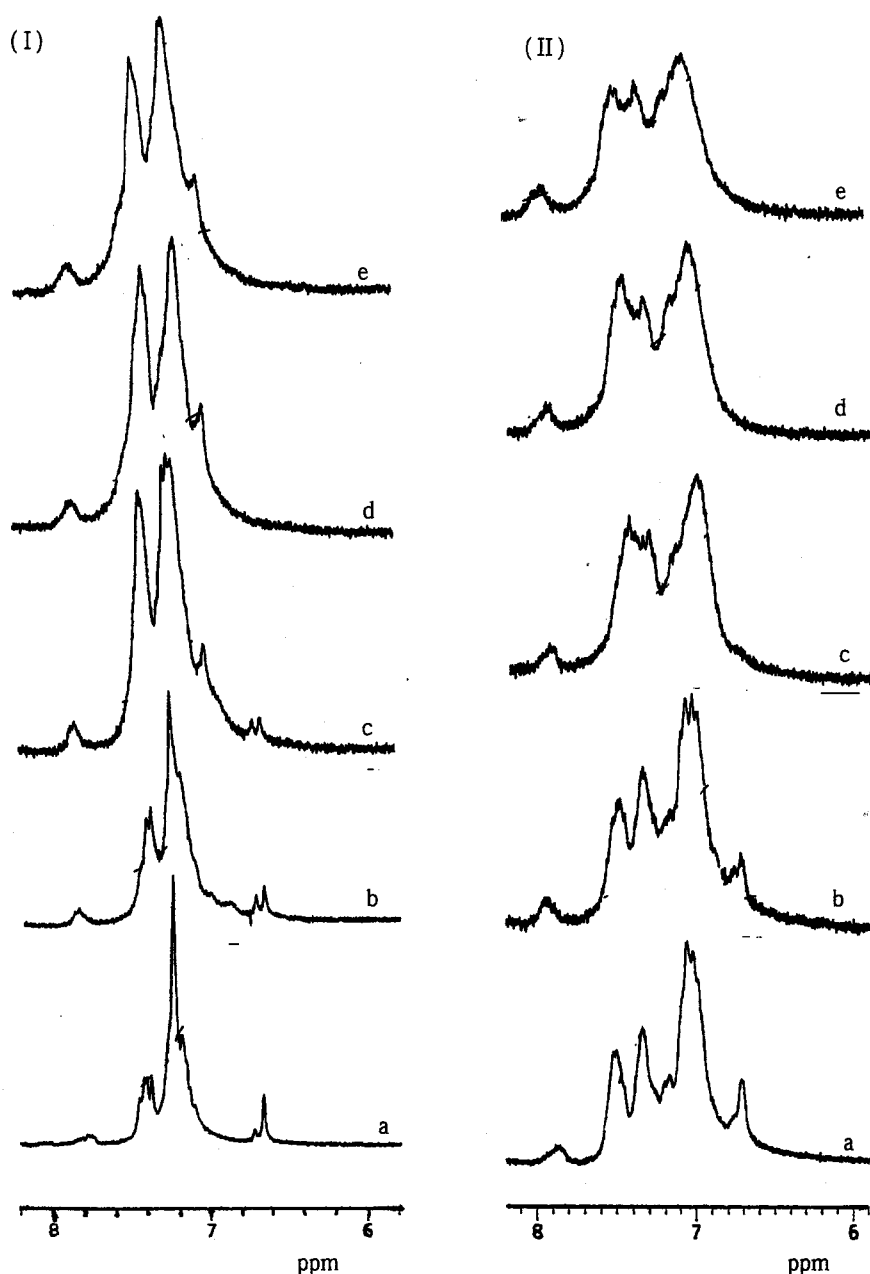


Figure 3. (I) ^1H NMR of CT complexes with increasing mol ratio of the repeating unit of **2a**: TCNQ; (a) 1:0.0, (b) 1:0.3, (c) 1:0.6, (d) 1:0.9 and (e) 1:1.5; (II) ^1H NMR of CT complexes with increasing mol ratio of the repeating unit of **2b**: TCNQ; (a) 1:0.0, (b) 1:0.3, (c) 1:0.6, (d) 1:0.9 and (e) 1:1.5.

In the ^1H NMR spectrum of **2b** without TCNQ, the benzylidene proton was observed at 6.71 ppm and the aromatic and the dithiafulvene ring protons appeared between 6.85 to 7.6 ppm. When the feed ratio of TCNQ was 0.3, the intensity of the peak at 6.71 ppm was found to decrease. On further addition of TCNQ (ratio 0.6), the peak at 6.71 ppm disappeared completely and peaks were observed only in the region at 6.8 to 7.7 ppm. The disappearance of the benzylidene proton and observation of signals due to the charge-transferred structure of dithiafulvene unit takes place around a

ratio of 0.6 in the case of **2b** and at 0.9 in the case of polymer **2a**. The early disappearance of the benzylidene proton in the case of **2b** might be due to the presence of the lone pair of electrons on the oxygen which leads to extended resonance with the dithiolium ion formed as a result of charge transfer. Thus, a partial charge transfer from all units of dithiafulvene of the polymer could be achieved through the resulting π -conjugated backbone even when the amount of mol percent of TCNQ added is less than one. In the case of **2a** at a feed ratio of added TCNQ equal to 0.6, presence of neutral units of dithiafulvene as well as the charge transferred dithiolium ion was inferred from NMR analysis.

In the ^1H NMR spectrum of the CT complex of **4a** with TCNQ at $[\text{TCNQ}]/[\text{repeating unit of } \mathbf{4a}] = 1.0$, the peaks due to the dithiafulvene unit at 6.12 ppm and 5.35 ppm had disappeared and new broad peaks were observed at 7.43 ppm and 6.3 ppm. The new peaks at 7.43 ppm and 6.3 ppm are attributed to the charge transferred dithiafulvene structure.

The IR spectra of the CT complexes of **2a** and **2b** with TCNQ showed a weak absorption at 2225 cm^{-1} , a strong absorption 2197 cm^{-1} and a medium absorption at 2182 cm^{-1} for **2** and similar absorptions at 2225 cm^{-1} , 2198 cm^{-1} and 2182 cm^{-1} for **2b**. Similarly for the CT complex of **4a** a weak absorption was observed at 2226 cm^{-1} , a strong absorption at 2198 cm^{-1} and a medium absorption at 2182 cm^{-1} . The peak at 2226 cm^{-1} is known to arise from neutral TCNQ and that at 2182 cm^{-1} due to TCNQ anion radical with peaks due to intermediate charge transferred state of TCNQ appearing between these two.¹⁵ These results imply that in the entire CT complexes neutral, partial charge transferred and completely charge transferred TCNQ units were present. The degree of charge transfer of the partial charge transferred TCNQ in **2a** and **4a** were 0.70 and 0.68, respectively.¹⁵

In the UV-vis spectra of the all CT complexes, major maxima were observed at 845 nm, 763 nm, and 745 nm (attributed to the anion radical of TCNQ) and at 395 nm (composite of neutral TCNQ and TCNQ anion radical)¹⁶ (Figure 4). When the molar ratio of the repeating unit of the polymer: TCNQ was increased from 1: 0.25 to 1:1, the absorbance at 845 nm which is due to the anion radical of TCNQ increased gradually reaching maximum at 1 : 1 along with a sharp increase in the absorbance at 395 nm. On further increasing the feed beyond 1 : 1, there were almost constant intensities in the absorbance at 845 nm with a small increase in the absorbance at 395 nm. From these results it was inferred that 1 : 1 complexes of the dithiafulvene unit : TCNQ are formed. Similar results had been obtained for the π -conjugated poly(dithiafulvene)s.¹⁷

Electrical conductivity was measured on films cast from DMSO for the aromatic poly(dithiafulvene)s and their CT complexes with TCNQ. The electrical conductivity was found to be $5.76 \times 10^{-4}\text{ S cm}^{-1}$ and $3.75 \times 10^{-7}\text{ S cm}^{-1}$ for undoped polymer **2a** and **2b** respectively. The value for their corresponding CT complexes with TCNQ was $1.68 \times 10^{-4}\text{ S cm}^{-1}$ (three orders of magnitude higher) and $1.79 \times 10^{-5}\text{ S cm}^{-1}$ (two orders of magnitude higher).

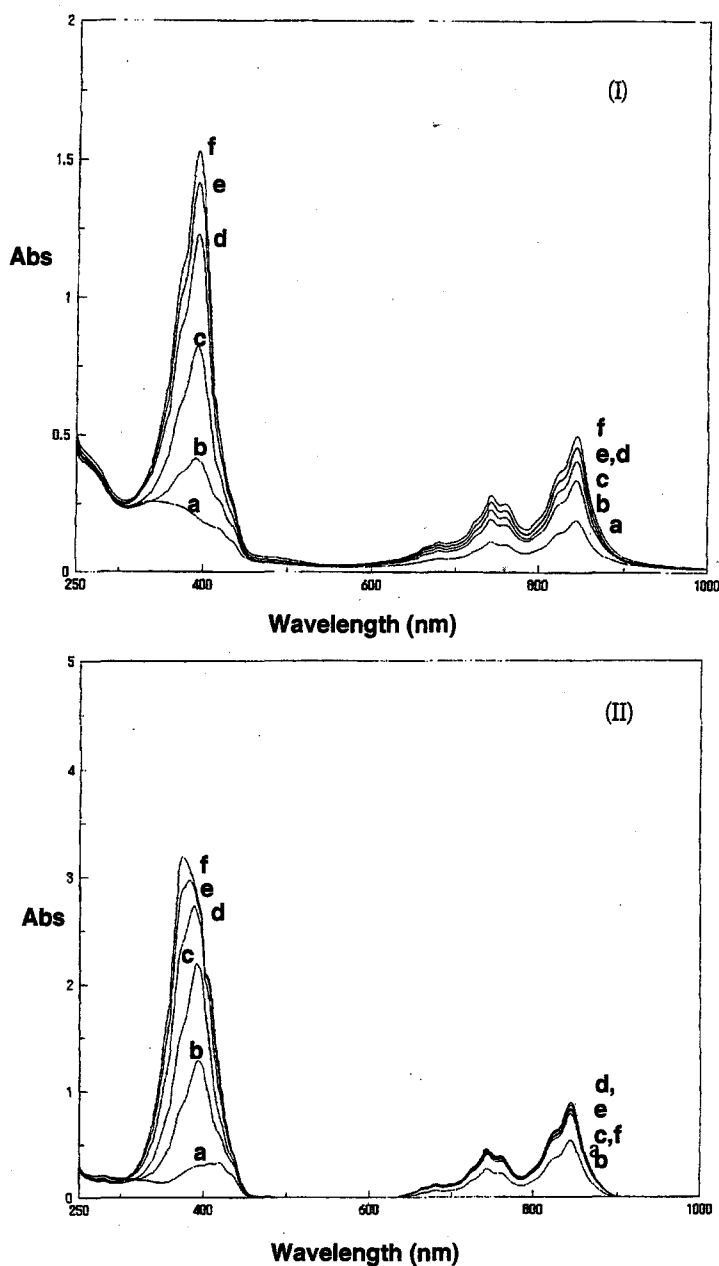


Figure 4. UV-vis spectra of CT complexes at different mol ratios of the repeating unit of polymer: TCNQ; (a) 1:0.25, (b) 1:0.5, (c) 1:0.75, (d) 1:1, (e) 1:1.25 and (f) 1:1.5; for **2b** (I) and **4a** (II).

The possibility of using methylene linked aromatic poly(dithiafulvene) (**2a**) as precursor polymers to small band-gap conducting polymers was investigated. It was tried to attempt oxidative dehydrogenation of **2a** by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which is an oxidative dehydrogenating agent for poly(heteroarylene methylene)s.⁹ Although an excess amount of DDQ was reacted with **2a**, the peak due to the π - π^* transition in the UV-vis absorption spectra of the reacting polymer was the same as that of the precursor polymer. In the ^1H NMR of **2a**, the intensity of the methylene proton resonance at 3.9 ppm did not decrease after **2a** was treated with DDQ. These results indicate that oxidative dehydrogenation of the

methylene-linked polymer by DDQ was unsuccessful. The oxidative dehydrogenation might be inhibited by formation of the CT complex of DDQ with the dithiafulvene unit in **2a**. The CT complex formation was confirmed by the fact that the peak at 6.65 ppm (benzylidene proton of the dithiafulvene unit) disappeared completely in the ^1H NMR of **2a** with DDQ.

Summary

The cycloaddition polymerization starting from the aromatic diynes resulted in the formation of the expected poly(dithiafulvene)s in reasonable yields. The cycloaddition polymerization starting from the aliphatic diynes resulted in low molecular weight poly(dithiafulvene)s along with side reactions leading to a high molecular weight fraction with the absence of the dithiafulvene structure. These results suggest that an aromatic thioketene intermediate favors the cycloaddition reaction. The methylene bridged aromatic poly(dithiafulvene) (**2a**) can be considered as an interesting precursor to an alternating aromatic and quinonoid structure containing small band gap semi-conducting polymer. Cyclic voltammetric studies showed that the oxidation potential was high in the case of the aliphatic poly(dithiafulvene) (1.30 V) and decreases in the aromatic poly(dithiafulvene)s. Between the two aromatic poly(dithiafulvene)s, **2b** has a lower oxidation potential (0.48 V) as compared to **2a** (0.60 V), presumably due to the ease of formation and higher resonance stabilization of the corresponding 1,3-dithiolium ion in case of the former.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under nitrogen. Bis(4-ethynyldiphenyl)methane (**1a**) and 4,4'-diethynyldiphenyl ether (**1b**) were prepared according to literature reports^{18,19} and purified by passing over a short column of silica gel using hexane as an eluent.

Measurements. IR spectra were recorded on a Perkin Elmer 2000 spectrometer. ^1H NMR spectra were recorded on a JEOL JNM EX-270 MHz instrument. Gel permeation chromatographic analysis was carried out on a TOSOH-8020 instrument using a TSH-GEL ALPHA 3000 column with DMSO containing 10 mM LiBr as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. For cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out using a BAS CV-50W voltammetric analyzer with a 0.1 M acetonitrile solution containing $(\text{NEt}_4)\text{BF}_4$ as an electrolyte. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. For electrical conductivity, thin polymer films were deposited on glass plates by casting from a DMSO solution. They were dried under vacuum. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 2400 source meter. For recording ^1H NMR, a 1:1 CT complex was prepared by dissolving 0.05 mmol of polymer and 0.05 mmol of TCNQ in $\text{DMSO}-d_6$. For UV-vis, poly(dithiafulvene) (0.05 mmol) was dissolved in 4 mL DMSO and incremental amount (2.5 mg) of TCNQ was added in steps to give ratios 1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.25 and 1:1.5. After each addition of TCNQ the solution was stirred for 10 min and 0.02 mL of the solution was taken in acetonitrile for analysis.

Synthesis of poly(dithiafulvene)s. A typical cycloaddition polymerization was carried out as follows. To a solution of **1a** (0.216 g, 1.00 mmol) in Et₂O (4 mL) was added a 1.6 M solution of n-butyllithium in hexane (1.25 mL, 2.00 mmol) at 0 °C. After the reaction mixture was stirred for 30 min, sulfur (0.064 g, 2.00 mmol) was added to the solution. The reaction mixture was stirred for 2 h and cooled to -30 °C, and water (0.036 mL, 2.00 mmol) was added dropwise and the temperature allowed to come up to room temperature. The reaction mixture was stirred for 3 h at room temperature to effect polymerization and finally piperidine (0.2 mL) was added to quench the terminal thioketenes. After the reaction mixture was stirred for 30 min, the mixture was poured into a large excess of Et₂O. The precipitate was washed with water to remove inorganic salts. The product was dried to give 0.15 g of an polymer (**2a**) (53 % yield). IR (KBr, cm⁻¹) 3403 (b, m), 1582 (sh, m), 1558 (sh, w), 1505 (sh, m), 1411 (sh, m). ¹H NMR (DMSO-*d*₆): δ 1.1-1.7 (CH₂ of piperidine unit), 3.6 (N-CH₂ of piperidine unit), 3.8-4.0 (Ph-CH₂-Ph), 4.0-4.3 (N-CH₂ of piperidine unit and CH₂C(=S)N<), 6.65 (>C=CH-Ph), 7.0-7.5 (dithiole ring and aromatic protons). Anal. Calcd for (C₁₇H₁₂S₂•0.5H₂O)_{14.0}•(C₂₇H₃₄N₂S₂): C, 70.61; H, 4.83; N, 0.64. Found: C, 69.68; H, 4.78; N, 0.62.

2b. 4,4'-Diethynyldiphenyl ether (**1b**) (0.218 g, 1 mmol) gave 0.16 g of polymer (**2b**) (56 % yield). IR (KBr, cm⁻¹) 3414 (b, m), 1588 (sh, m), 1548 (sh, w), 1495 (sh, m), 1239 (sh, s), 1170 (sh, m). ¹H NMR (DMSO-*d*₆): δ 1.1-1.7 (CH₂ of piperidine unit), 3.6 (N-CH₂ of piperidine unit), 4.0-4.3 (N-CH₂ of piperidine unit and CH₂C(=S)N<), 6.71 (>C=CH-Ph), 6.8-7.6 (dithiole ring and aromatic protons). Anal. Calcd for (C₁₆H₁₀OS₂)_{12.9}•(C₂₆H₃₂N₂OS₂): C, 68.16; H, 3.96; N, 0.68. Found: C, 68.40; H, 4.06; N, 0.67.

4a. 1,7-Octadiyne (**3a**) (0.26 mL, 2 mmol) with THF (8 mL), n-BuLi (4 mmol), sulfur (4 mmol), and water (4 mmol) gave 0.11 g of polymer (**4a**) (32 % yield). IR (KBr, cm⁻¹) 3392 (b, m), 2924 (sh, m), 1624 (b, m), 1571 (b, m), 1519 (sh, m), 1439 (sh, m), 1125 (b, w), 1000 (sh, w), 865 (sh, w). ¹H NMR (DMSO-*d*₆): δ 1.1-2.4 (m, aliphatic protons), 4.18 (N-CH₂ of piperidine unit), 5.35 (s, -HC=C(S)S), 6.18 (s, -S-CH=C(S)C).

4b. 1,9-Decadiyne (**3b**) (0.33 mL, 2 mmol) with THF (8 mL), n-BuLi (4 mmol), sulfur (4 mmol), and water (4 mmol) gave 0.155 g of polymer (**3b**) (40 % yield). IR (KBr, cm⁻¹) 3402 (b, m), 2926 (sh, m), 2853 (sh, w), 1634 (b, m), 1574 (sh, w), 1432 (b, w). ¹H NMR (DMSO-*d*₆): δ 1.0-2.2 (m, aliphatic protons), 4.18 (N-CH₂ of piperidine unit), 5.38 (s, -HC=C(S)S), 6.18 (s, -S-CH=C(S)C).

Synthesis of CT complexes of poly(dithiafulvene)s with TCNQ. Poly(dithiafulvene) (0.05 mmol) was dissolved in DMSO (1 mL) and TCNQ (0.05 mmol) was added to it. An intense green solution was formed. The solution was filtered and DMSO was pumped off to give a dark powder.

CT complex with 2a. IR (KBr, cm⁻¹) 3422 (b, m), 2226 (sh, w), 2198 (sh, m), 2182 (sh, m), 2168 (sh, w), 1710 (b, w), 1579 (sh, m), 1505 (sh, m), 1416 (sh, w), 1338 (b, w), 1134 (sh, m), 1021 (sh, w).

CT complex with 2b. IR (KBr, cm⁻¹) 3416 (b, m), 2226 (sh, w), 2197 (sh, m), 2182 (sh, m), 2169 (sh, w), 1579 (sh, m), 1497 (sh, m), 1338 (b, w), 1243 (sh, m), 1182 (sh, m), 1015 (sh, w).

CT complex with polymer 4a. IR (KBr, cm⁻¹) 3407 (b, m), 2226 (sh, w), 2198 (sh, m), 2182 (sh, m), 2168 (sh, w), 1578 (sh, m), 1509 (sh, m), 1337 (b, w), 1182 (sh, m), 1133 (sh, w), 1021 (sh, w).

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Part II

Poly(dithiafulvene)s toward Functional Materials

Chapter 6

A Polymer with Two Different Redox Centers in the π -Conjugated Main Chain: Alternate Combinations of Ferrocene and Dithiafulvene

Abstract: A redox active alternating π -conjugated copolymer of ferrocene with dithiafulvene was synthesized by cycloaddition polymerization of aldothioketene derived from 1,1'-bis(trimethylsilylethynyl)ferrocene (**1**). The obtained polymer (**2**) was soluble in common organic solvents such as THF, CH_2Cl_2 , CHCl_3 , DMF, and DMSO. The structure of **2** was confirmed by IR, ^1H and ^{13}C NMR spectra compared with those of 2,6-bis(ferrocenyl)-1,4-dithiafulvene as a model compound (**3**). The cyclic voltammogram of **3** showed three oxidation peaks, which were originated from the two ferrocene units and the dithiafulvene unit. The polymer **2** showed only single-broad oxidation peak at 0.58 V vs. Ag/Ag^+ . This result was caused by an effective interaction between two different donors in **2**. The compounds **2** and **3** did not undergo oxidative dimerization to form extended tetrathiafulvalene during cyclic voltammetry. The polymer **2** formed a soluble charge-transfer (CT) complex with TCNQ in DMSO. The ratio of the dithiafulvene unit in **2** to TCNQ in the complex was 1:1, confirmed by ^1H NMR. The electrical conductivity of **2** was 3.6×10^{-3} S/cm after I_2 doping.

Introduction

The study of molecules comprising two different redox centers that are covalently linked is a developing area within supramolecular chemistry, with application in molecular electric devices, sensors, electrocatalysis and energy conversion.¹ Current research in this area focuses on gaining control over charge-transfer (CT) interactions between combinations of organic and organometallic species, e.g., bipyridinium cations, quinones, metallocenes and metal-coordinated macrocycles.² Combinations of ferrocene with multisulfur compounds offer new sulfur-based synthon for the preparation of molecular materials with unusual properties such as enhanced electrical conductivity, unusual magnetic behavior and non-linear-optical (NLO) effects.³ Ferrocenyldithiafulvene compounds have been studied to achieve new attractive materials in such fields.⁴ Ueno et al. reported that diferrocenyltetrathiafulvalene formed 1:1 CT complex with 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ), with electrical conductivity of $1 \times 10^{-3} \text{ S/cm}$.^{4a}

Incorporation of dithiafulvene derivatives into π -conjugated polymer backbones is an attractive subject because of the enhanced processabilities of their charge transfer salts and/or the anticipated high electrical conductivities.⁵ The author has developed the synthesis of new π -conjugated polymers having dithiafulvene and aryl units alternately in the main chain.⁶ The UV-vis absorption spectra and cyclic voltammetry measurements of the polymers showed effective expansions of the π -conjugation systems in the polymers.^{6a,b} These polymers formed soluble CT complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ).^{6a,c}

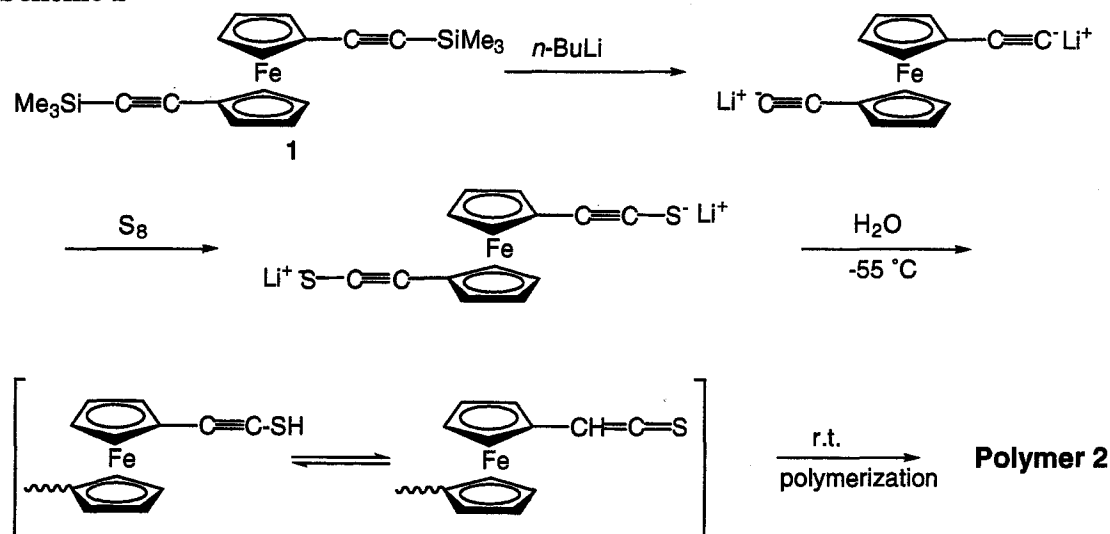
In this chapter, the author describes the synthesis of an alternating copolymer of dithiafulvene with ferrocene units by cycloaddition polymerization of ferrocenyl thioketene. Both dithiafulvene and ferrocene units are electron donors. Incorporation of two different donors into main chains of π -conjugated system should be interesting. No example of the polymers containing the combination of dithiafulvenes and ferrocenes in π -conjugated systems has been reported. The author has found that electrochemical analysis for this new polymer showed an interesting behavior compared with its model compound.

Results and Discussion

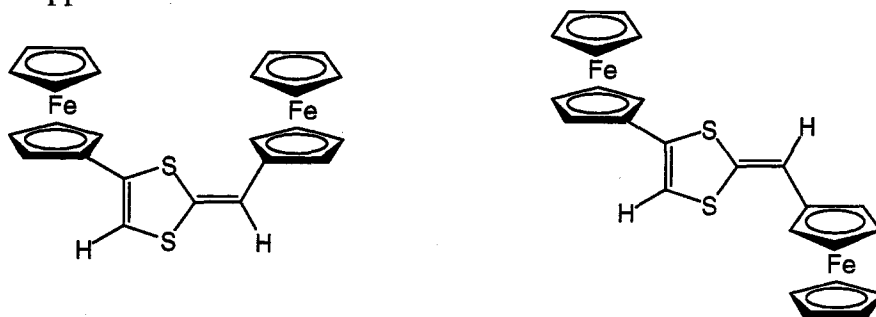
1,1-Diethynylferrocene, which is an ideal monomer to generate an aldothioketene reactant, is unstable to be isolated. A stable trimethylsilane derivative **1** can be prepared via an unstable diethynylferrocene by treatment of diacetylferrocene using Negishi's method.⁷ **1** undergoes electrophilic substitution reactions to give various compounds in good yield, so that the polymerization reaction was tried to be carried out from **1** instead of 1,1-diethynylferrocene. Scheme 1 provides the outline of polymerization by cycloaddition reaction of aldothioketene with alkynethiol tautomer derived from monomer **1**.^{6a,b,8} To a solution of **1** in THF, *n*-butyllithium was added at -78°C . The reaction mixture was slowly warmed to ambient temperature and stirred overnight. After treated with sulfur and an equimolar of water as a proton source, the reaction mixture was stirred for 3 h to effect polymerization. The mixture was then poured into a large quantity of *n*-hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a brown-colored polymer **2** was obtained (50 % yield). The polymer **2** was soluble in common organic solvents such as THF, CH_2Cl_2 , CHCl_3 , DMF, and DMSO. The molecular weight

measurement was performed by GPC in eluent CHCl_3 . The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of **2** were $M_n = 1930$ and $M_w/M_n = 1.33$, respectively.

Scheme 1



The model compound **3** was prepared from ethynylferrocene to determine the structure of the polymer **2**. The structure of **3** was confirmed by IR, ^1H and ^{13}C NMR spectra. In the IR spectrum of **3**, a peak appeared at 1559 cm^{-1} was due to a $\text{C}=\text{C}$ vibration of the dithiafulvene moiety. The ^1H NMR spectrum of **3** showed two peaks assigned to dithiafulvene protons at 5.60 and 6.10 ppm. The former peak was corresponding to the ylide proton, the latter is for the dithiole proton. In the ^{13}C NMR spectrum, eight peaks attributed to four dithiafulvene carbons were observed at 108.4, 109.0, 110.5, 110.9, 131.5, 131.7, 132.9 and 133.1 ppm, indicating the model compound **3** was a mixture of *E* and *Z* isomers. The reaction mechanism of cycloaddition of aldothioketenes with their alkynethiol tautomer supports the predominant formation of *Z* isomers.^{6b,8d,e} The ratio of the *E* to the *Z* isomer of **3** was estimated to be 1 to 2 from comparison of intensities of the peak area at 110.5 ppm with that at 110.9 ppm.



Z-3

E-3

The IR and ^1H NMR spectra of **2** were similar to those of **3**. The IR spectrum of **2** showed a peak at 1560 cm^{-1} assigned to the dithiafulvene unit. A weak

peak at 2153 cm^{-1} was assigned to a $\text{C}\equiv\text{C}$ vibration of the unreacted terminal trimethylsilylethynyl group. Figure 1 shows the ^1H NMR spectrum of **2**, which exhibited two extremely broad peaks around 5.6 and 6.2 ppm attributed to dithiafulvene protons. This type of broadening was also observed in the spectra of the π -conjugated poly(dithiafulvene)s previously reported.^{6a,b} A broad peak was observed at 0.24 ppm, which was assigned to the terminal trimethylsilyl moiety. The degree of polymerization (DP) was estimated by the comparison of the intensities of the absorptions of the ferrocene protons in the repeating unit with those of the absorption of the terminal trimethylsilyl protons. The value of DP was 5.5 ($M_n = 2020$), which was consistent with the value from GPC data. In the ^{13}C NMR spectrum of **2**, broad peaks for the dithiafulvene carbons were recognized around 109 and 128 ppm, and a peak at 0.83 ppm due to the carbons of the terminal trimethylsilyl group was also observed. Table 1 summarizes the results of the polymerization under various conditions. When the reaction was attempted in Et_2O , no polymeric product was obtained (entries 1 and 2). The use of hexamethylphosphorus triamide (HMPT), which is a favorable solvent for nucleophilic substitution reactions,⁷ decreased both the yield and the molecular weight of the product (entry 4). This relatively low reactivity of the trimethylsilylethynyl group toward $n\text{-BuLi}$ caused the low molecular weight of the polymer **2**.

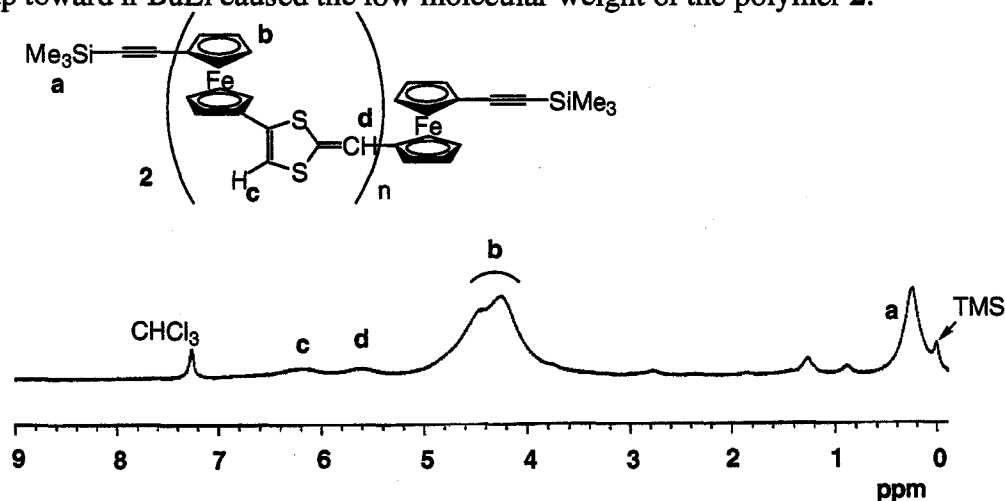


Figure 1. ^1H NMR spectrum of **2** in CDCl_3

Table 1. Preparation of Polymer **2** under Various Conditions

entry	solvent	nucleophile	yield (%)	M_n^b	M_w^b	M_w/M_n^b
1	Et_2O	MeLi	no			
2	Et_2O	$n\text{-BuLi}$	no			
3	THF	$n\text{-BuLi}$	50	1930	2570	1.33
4	THF-HMPT ^a	$n\text{-BuLi}$	27	990	2200	2.23

^a The ratio of THF to HMPT (hexamethylphosphorus triamide) was 1 to 0.3. ^b Determined from GPC.

Figure 2 shows the UV-vis absorption spectra of **2** and **3** in CHCl_3 . The compound **3** showed a peak at 450 nm, assignable to a d-d transition in the ferrocene unit⁹ and a strong absorption peak due to $\pi\text{-}\pi^*$ transition at 303 nm. Although the

π - π^* absorption band of **2** showed no obvious peak, relatively broad absorption spectrum was observed in comparison with that of **3**. This might indicate some conjugative interaction within the unit structure.

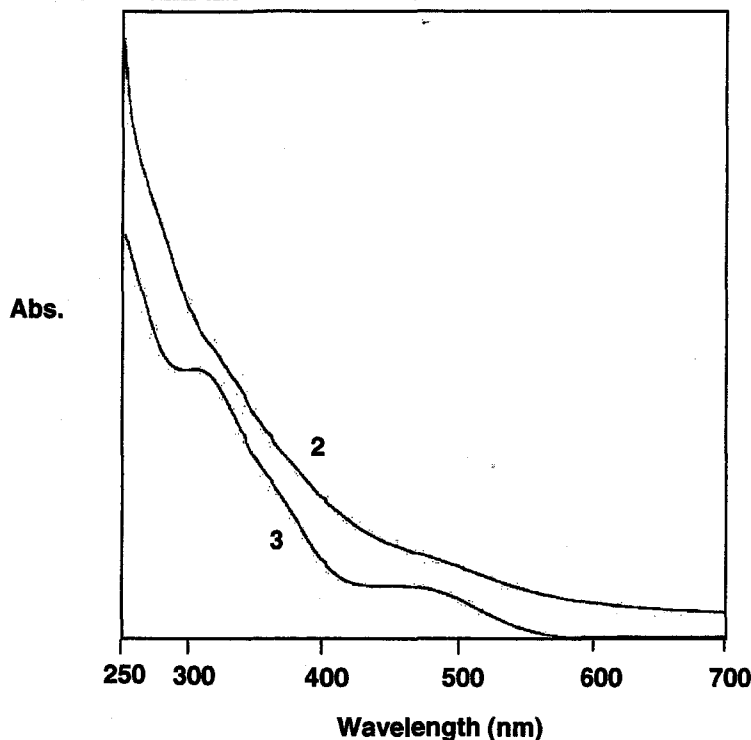


Figure 2. UV-vis absorption spectra of **2** and **3** in CHCl_3 .

The redox properties of **2** and **3** were studied by cyclic voltammetry. The model compound **3** exhibited three reversible oxidation peaks at 0.21, 0.50 and 0.85 V vs Ag/Ag^+ , which were originated from the two ferrocenes and the dithiafulvene. In the literature, the intermolecular oxidative dimerizations of 1,4-dithiafulvenes to yield the dication of the corresponding extended tetrathiafulvalene (TTF) systems were reported.¹⁰ In these cases, a reversible wave appears at less positive potential during the reverse cathodic scan when the oxidation peak of the dithiafulvenes has been scanned beforehand. This result shows that during the scan, the oxidation of the dithiafulvenes led to the formation of the dimer TTFs which are oxidized at less positive potentials than the dithiafulvenes. It should be noted that such a dimerization of ferrocene system **3** was not observed during cyclic voltammetry. On repeated cycling of the voltammogram of **3**, there was no marked change in the trace and no evidence was obtained for the formation of corresponding TTF. Moore et al. have reported that ferrocenyl dithiafulvenes (**4**) did not undergo the dimerization reaction during cyclic voltammetry.^{4d} Both results were due to the ferrocenyl substituent of **3** and **4** increasing the stability of the derived cation radical to the extent that they were significantly more stable than anticipated. It is known that α -ferrocenylcarbonium cations **5** are unusually stable.¹¹ The electron transfer level of **3** during the CV measurement was estimated from the electric current compared with that of ferrocene as a standard. The peaks x, y and z involved 0.17, 0.67 and 0.20 electron transfer, respectively.

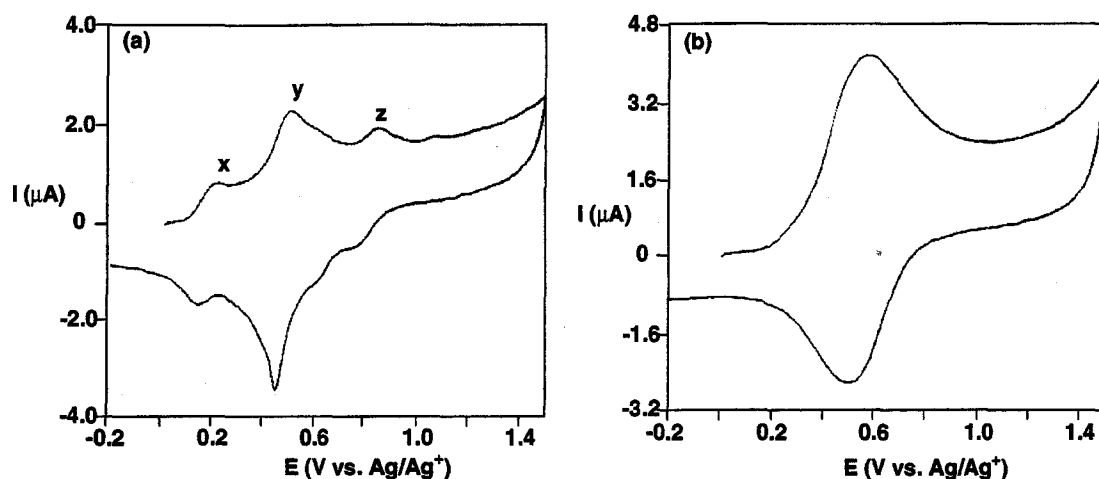
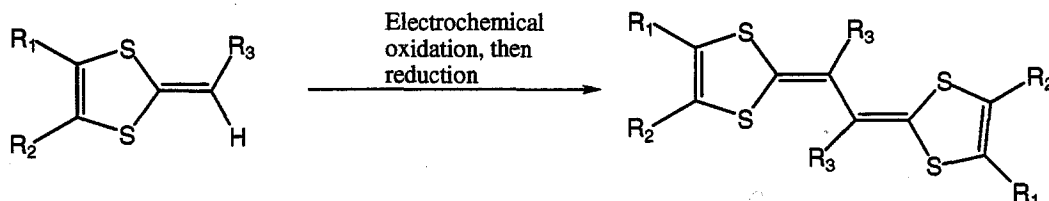


Figure 3. Cyclic voltammograms of (a) **3** and (b) **2**, measured in CH_2Cl_2 solution of 0.2 M tetrabutylammonium hexafluorophosphate at 300mV/s.

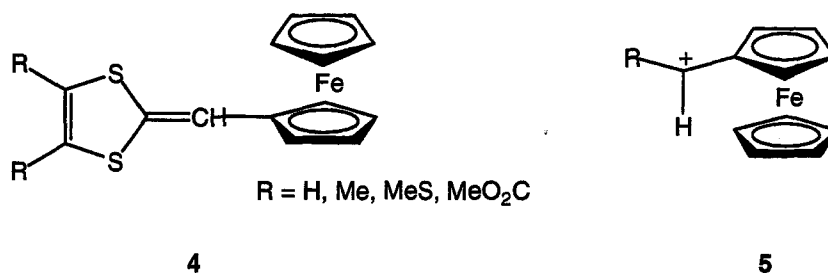
Redox behavior of **2** was found to be quite unique. As mentioned above, **3** exhibited three reversible oxidation peaks due to its three different redox sites. The compounds **4** showed expected two oxidation peaks.^{4d} Although **2** had two kinds of donors in the main chain, the cyclic voltammogram of **2** showed only single-broad oxidation peak at 0.58 V vs. Ag/Ag^+ . A corresponding reduction peak occurs at 0.50 V vs. Ag/Ag^+ . This new observation should result from an effective interaction between two donors in **2** in contrast to the model compounds **3** and **4**. To the best of our knowledge, this was the first redox behavior resulted from such a combination of donors. The positive charge stored by the repeating unit during CV scan was estimated by use of ferrocene standard. The peak at 0.58 V involved 1.21 electron transfer, suggesting an effective charge transfer from the repeating unit during the scan. Non-conjugated dithiafulvenes are typically oxidized to the cation radical at between $E^{\text{ox}} + 0.9$ and $+1.4$ V, depending on their substituents. The low potentials of the oxidation peaks of **2** and **3** are consistent with a highly delocalized π -electron system, as observed previously when π -conjugation of dithiafulvene derivatives is extended.^{6a,b,9e,f,12} Similarly to the model compound **3**, no sign for the dimerization of dithiafulvene unit of **2** was obtained during cyclic voltammetry. This fact showed the high stability of **2** against the oxidation, resulting in no inter- and/or intramolecular dimerization of the dithiafulvene unit.

Scheme 2



The polymer **2** formed CT complex with TCNQ in DMSO similarly to the π -conjugated poly(dithiafulvene)s previously reported.^{6a,c} The obtained CT complex was soluble in DMSO, DMF, acetonitrile and acetone, and partially soluble in THF. The ratio of dithiafulvene unit to TCNQ in the CT complex was determined by ^1H NMR

spectrum of the sample. The ^1H NMR spectrum after an excess amount of TCNQ was added to the $\text{DMSO}-d_6$ solution of **2** showed a broad peak around aromatic region assignable to the protons of dithiafulvene unit of **2** and TCNQ. The reason for these broad signals might be due to the complex having paramagnetic species. The peaks for unreacted TCNQ hardly appeared in the ^1H NMR spectrum due to its limited solubility in DMSO. Comparison of the intensity of the absorption of the aromatic region with that of the ferrocenyl region showed the complex containing about 1:1 ratio of the dithiafulvene unit to TCNQ. The UV-vis absorption of the CT complex exhibited major maxima at 845, 762 and 745 nm, indicating an anion radical of TCNQ in the sample. The electrical conductivity of the CT complex was $5.0 \times 10^{-6} \text{ S/cm}$ at room temperature. After doped with iodine, the polymer **2** showed the conductivity of $3.6 \times 10^{-3} \text{ S/cm}$.



Summary

New type of dithiafulvenes of **2** and **3** with appended ferrocenyl substituents were synthesized by cycloaddition of aldothioketenes. The author succeeded to carry out the polymerization from **1** of which acetylene moieties were protected by trimethylsilane. In contrast to the previous report, the oxidative dimerizations of **2** and **3** were not observed during cyclic voltammetry. These results suggest that ferrocenyl substituents stabilized intermediate radical cations of dithiafulvenes in **2** and **3** for the oxidative dimerization. The cyclic voltammogram of **2** showed only one reversible potential due to effective interaction within the unit structure. The polymer **2** formed the soluble CT complex with TCNQ in DMSO. The conductivity of **2** showed $3.6 \times 10^{-3} \text{ S/cm}$ after doped with iodine.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2 . 1,1'-Bis(trimethylsilylethynyl)ferrocene and ethynylferrocene were synthesized according to the literature.⁷

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. IR spectrum was recorded on a Perkin Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography was carried out on a Shodex K-803 by using chloroform as an eluent after calibration with standard polystyrene samples. Cyclic voltammetry was recorded on a BAS CV-50W Electrochemical Analyzer. The experiments were carried out in CH_2Cl_2 solution of the compound containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Electrical conductivity was measured

at room temperature by two-probe technique using a Keithley 2400 source meter.

Polymerization. To a solution of 1,1'-bis(trimethylsilylethynyl)ferrocene (189 mg, 0.50 mmol) in THF (1.0 ml), 1.6 M solution of n-butyllithium in hexane (0.65 ml, 1.04 mmol) was added at -78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. The temperature of the mixture was cooled at 0 °C. After adding the powder of sulfur (32 mg, 1.00 mmol), the reaction mixture was stirred for 2 h at 0 °C, then cooled at -55 °C and water (18 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. The mixture was then poured into a large quantity of n-hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a brown-colored polymer **2** was obtained (74 mg, 50 % yield). ¹H NMR (CDCl₃); δ 0.24 (-TMS), 3.8-4.9 (ferrocenyl protons), 5.6 (dithiafulvene), 6.2 (dithiafulvene); IR (KBr, cm⁻¹) 2153, 1560, 1548, 1434, 1252, 1038, 845.

Model Compound (2,6-Bis(ferrocenyl)-1,4-dithiafulvene) (3). To a solution of ethynylferrocene (210 mg, 1.00 mmol) in THF (1.5 ml), 1.6 M solution of n-butyllithium in hexane (0.65 ml, 1.04 mmol) was added at -78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. The temperature of the mixture was cooled at 0 °C. After adding the powder of sulfur (32 mg, 1.00 mmol), the reaction mixture was stirred for 2 h at 0 °C, then cooled at -55 °C and water (1 ml) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 0.5 h. The organic layer was extracted with CH₂Cl₂ and dried over MgSO₄. After evaporation of the solvent, the obtained solid was recrystallized from toluene/hexane. (123 mg, 51 % yield). ¹H NMR (benzene-*d*₆); δ 3.97 - 4.23 (m, 14H), 4.31 (m, 2H), 4.42(m, 2H), 5.62 (s, 1H), 6.08 (s, 1H); ¹³C NMR (benzene-*d*₆); 67.0, 67.2, 67.4, 68.5, 68.8, 69.0, 69.4, 70.2, 70.5, 78.7, 79.3, 83.9, 84.0, 108.4, 109.0, 110.5, 110.9, 131.5, 131.7, 132.9, 133.1; IR (KBr, cm⁻¹); 1559, 1410, 1242, 1001, 843. Anal. Calcd: C, 59.53; H, 4.16. Found: C, 59.02; H, 4.05.

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Chapter 7

Alternating π -Conjugated Copolymer of Dithiafulvene with 2,2'-Bipyridyl Units

Abstract: A π -conjugated polymer containing a dithiafulvene unit and a bipyridyl unit was prepared by cycloaddition polymerization of aldothioketene derived from 5,5'-diethynyl-2,2'-bipyridine. The UV-vis absorption spectra showed that the π -conjugation system of the polymer expanded more effectively than that of a benzene analogue of a poly(dithiafulvene) obtained from 1,4-diethynylbenzene. Cyclic voltammetry measurement indicated the dithiafulvene-bipyridyl polymer as a weaker electron donor polymer than the benzene analogue. These results agreed that the incorporation of the electron accepting bipyridyl moiety into the conjugated poly(dithiafulvene) induced an intramolecular charge-transfer (CT) effect between the units. Treatment of the dithiafulvene-bipyridyl polymer with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ afforded a ruthenium polymer complex. Cyclic voltammogram of the complex showed broad redox peaks, which indicated the electronic interaction between the dithiafulvene and the tris(bipyridyl) ruthenium complex. The dithiafulvene-bipyridyl polymer formed CT complexes with TCNQ in DMSO. The UV-vis absorption indicated that the resulting CT complex contained anion radical of TCNQ and partially charge transferred TCNQ. The polymer showed an unusual high electrical conductivity of $3.1 \times 10^{-4} \text{ S/cm}$ in its non-doped state due to the effective donor-acceptor interaction between the bipyridine unit and the dithiafulvene unit.

Introduction

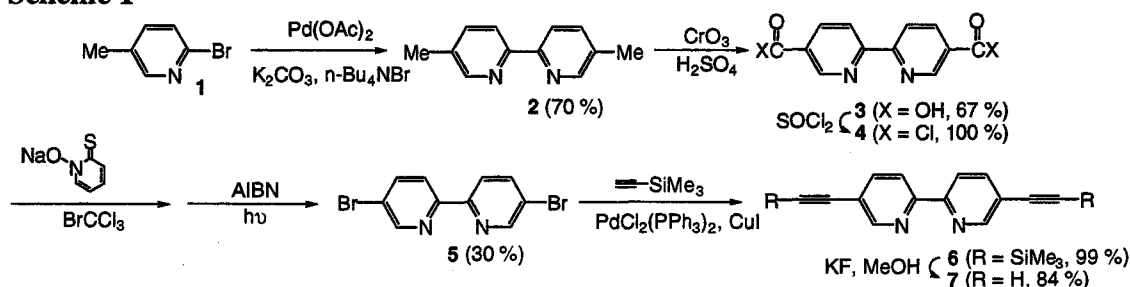
There has been growing interest in a new type of redox polymer that is a hybrid of materials containing both organic and inorganic components.¹ One of the most attractive systems is an incorporation of transition metal complexes into conjugated polymers, which provides enormous opportunities to tune the physical properties of the resulting materials. The key feature of these materials is that the metals are coordinated directly to the conjugated backbones of the polymers, or form a link in the backbones by electronic interaction between the electroactive metal centers and the electroactive polymer units. Consequently, this can lead to materials with a wide range of interesting properties, such as photorefractive effects, photoconductivity, and novel redox properties.^{1a-f} Oligopyridines have extensively been used as fundamental metal binding sites in this kind of systems due to their rich and well-characterized photophysics and redox chemistry.² Preparation of oligopyridine-metal complexes is of particular relevance in many fields of research for energy transfer processes, sensors, nonlinear optics, electroluminescence, and metal-ion-induced self-assembling phenomena.^{1g-o}

Pyridine structures are regarded as electron acceptors and polypyridines show n-doping property.^{1h,3} Alternate combination of a donor unit and an acceptor unit in a π -conjugated polymer chain enhances the π -conjugation system and the conductivity of the polymer and changes the redox property.⁴ Here the author describes the synthesis and properties of a π -conjugated polymer with 2,2'-bipyridine and electron donating dithiafulvene units as a series of the poly(dithiafulvene)s⁵.

Results and Discussion

Scheme 1 outlines the approach to the synthesis of a bipyridyl monomer. Homocoupling of **1** produced bipyridyl compound **2** by use of $\text{Pd}(\text{OAc})_2$ as a catalyst.⁶ After oxidation of **2** by $\text{CrO}_3/\text{H}_2\text{SO}_4$,⁷ the obtained dicarboxylic acid **3** was converted to the dichlorocarbonyl compound **4**.⁸ Barton's radical decarboxylative bromination was employed for the synthesis of **5**. Reaction of **4** with pyrrhione sodium salt in BrCCl_3 yielded an intermediate ester, which was photolyzed *in situ* to give dibromobipyridine **5** by a radical chain reaction.⁹ Pd-catalyzed cross-coupling reaction between **5** and (trimethylsilyl)acetylene provided **6**. Removal of the trimethylsilyl group by KF/MeOH yielded diethynyl compound **7**.¹⁰

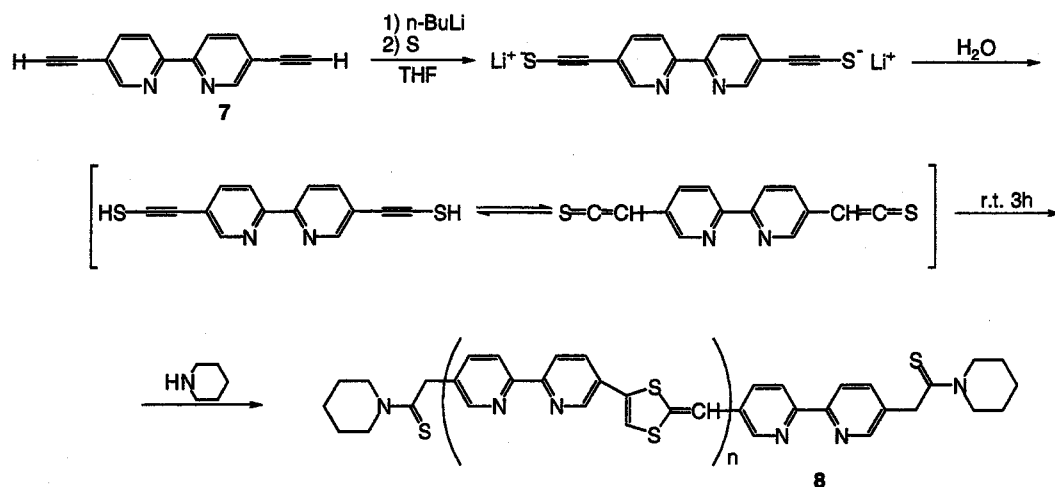
Scheme 1



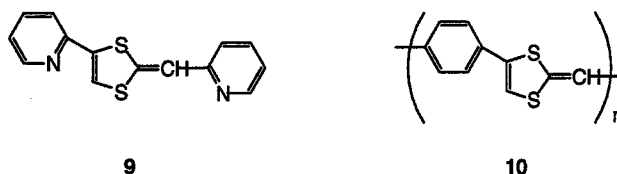
The author carried out the cycloaddition polymerization of aldothioketene with its alkynethiol tautomer derived from monomer **7**, according to our previous studies⁵ (Scheme 2). A π -conjugated poly(dithiafulvene) with 2,2'-bipyridine unit (**8**) was obtained after conversion of the terminal reactive thioketenes to the stable thioamide

moieties by treatment with piperidine (88 % yield). The polymer **8** was soluble in DMSO and partially soluble in CH₃CN, MeOH, acetone and DMF. The molecular weight measurement of **8** was performed by GPC in eluent DMSO with poly(ethylene oxide) standards. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were 8250 and 1710, respectively. The molecular weight distribution (M_w/M_n) of the polymer was 4.83.

Scheme 2



The model compound **9** was prepared^{5c} from 2-ethynylpyridine to determine the structure of the polymer **8**. In the IR spectrum of **9**, peaks corresponding to the double bonds of the dithiafulvene moiety appeared at 1582 and 1557 cm⁻¹. The IR spectrum of **8** showed same peaks for the repeating dithiafulvene units at 1575 and 1558 cm⁻¹. The ¹H NMR spectrum of **8** was similar to that of the model compound **9**. In the ¹H NMR spectrum of **8**, a broad peak for the benzylic proton appeared at 6.8 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.4 ppm. The ¹H NMR spectrum of **8** also showed two small broad peaks at 4.3 and 3.7 ppm attributed to the terminal thioamide moiety. The degree of polymerization (DP) was 8.8 (M_n = 2800), estimated by the comparison of the NMR peak intensities between the aromatic moiety and the terminal thioamide moiety.



The redox property of **8** was studied by cyclic voltammetry. The polymer **8** was electrochemically active and its cast film gave an irreversible oxidation peak due to the electron donating dithiafulvene moiety at 0.98 V vs. Ag/Ag⁺ in the cyclic voltammogram (Figure 1a). The cast film of **10** as the benzene analogue has been reported to give an oxidation peak at 0.61 V vs. Ag/Ag⁺.^{5b} The lower donating ability of **8** compared with that of **10** should result from the attachment of the electron accepting bipyridyl unit with the dithiafulvene unit. This combination offered a possible intramolecular charge-transfer (CT) effect between the units. Since the donor unit was incorporated into the π -conjugated main chain, the anodic shift of the oxidation

peak of **8** was observed compared with that of the model compound **9** ($E_{pa} = 0.45$ V).⁵ The irreversibility of the peak of **8** was caused by the oxidative dimerization of the dithiafulvene unit during the anodic scan, which was observed in other dithiafulvenes.^{5a-c,11} During the repeated scans of **8**, a reversible new wave appeared at a less positive potential of the oxidation peak for the dithiafulvene unit. This new redox peak is corresponding to a tetrathiafulvalene vinylogue resulted from the oxidative dimerization of the dithiafulvene unit. The polymer sample became insoluble after the repeated CV scans, suggesting that an inter- and/or intra-molecular dimerization of the dithiafulvene unit of **8** led to a cross-linking of the polymer. Electrochemical study of polybipyridines by Yamamoto group showed that a non-substituted polybipyridine had a sharp reduction peak at -2.2 V in the cyclic voltammogram.^{1h} In the case of **8**, no distinct peak for the bipyridine moiety appeared during the cathodic scan from 0 to -2.3 V (Figure 1d). The reduction peak corresponding to the bipyridyl unit in **8** should be shifted to out of the potential window due to the CT structure.

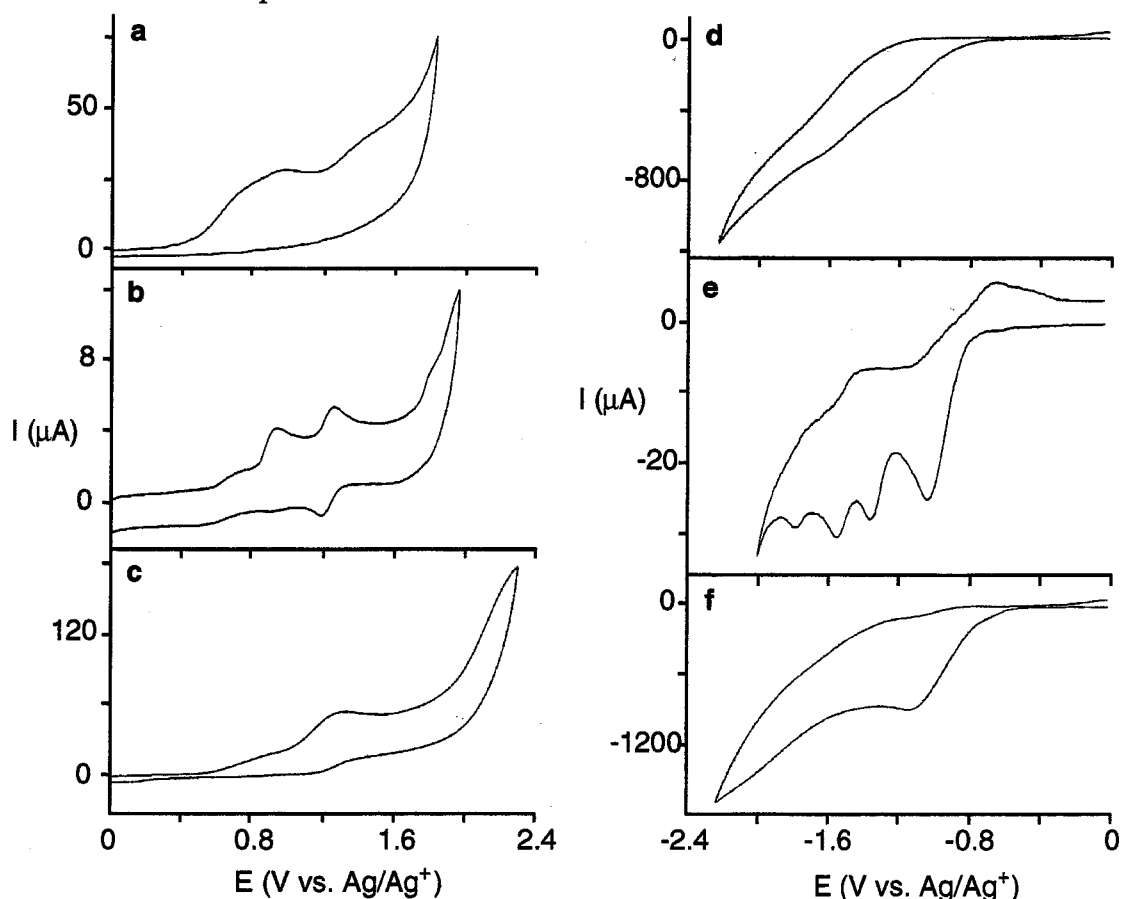


Figure 1. Cyclic voltammograms of (a) film of **8**, (b) [Ru(bpy)₃]Cl₂ and (c) film of **8**-ruthenium complex in anodic scan in CH₃CN solution containing 0.1 M [NEt₄]BF₄ and (d) film of **8**, (e) [Ru(bpy)₃]Cl₂ and (f) film of **8**-ruthenium complex in cathodic scan in CH₃CN solution containing 0.1 M [N(n-C₄H₉)₄]Br. Scan rates were 100 mV/s.

The UV-vis absorption spectra of **8**, the model compound **9**, and the benzene analogue **10**^{5a,b,d} ($M_n = 5440$) in DMSO are shown in Figure 2. The peak due to the π - π^* transition of **8** ($\lambda_{max} = 411$ nm) was located at a longer wavelength than that of **9**

($\lambda_{\text{max}} = 384 \text{ nm}$), indicating an effective development of π -conjugation system of **8**. Although the molecular weight of **8** was smaller than that of **10** of which π - π^* absorption was observed at 398 nm, the π -conjugation through the bipyridyl moiety was more expanded than that through the benzene moiety. The expanded π -conjugation in **8** was caused by an intramolecular charge-transfer (CT) interaction between the dithiafulvene and the bipyridyl units, which was supported by the CV results as described above. The peak intensity of the absorption in **8** was proportional to the concentration of the sample solution.

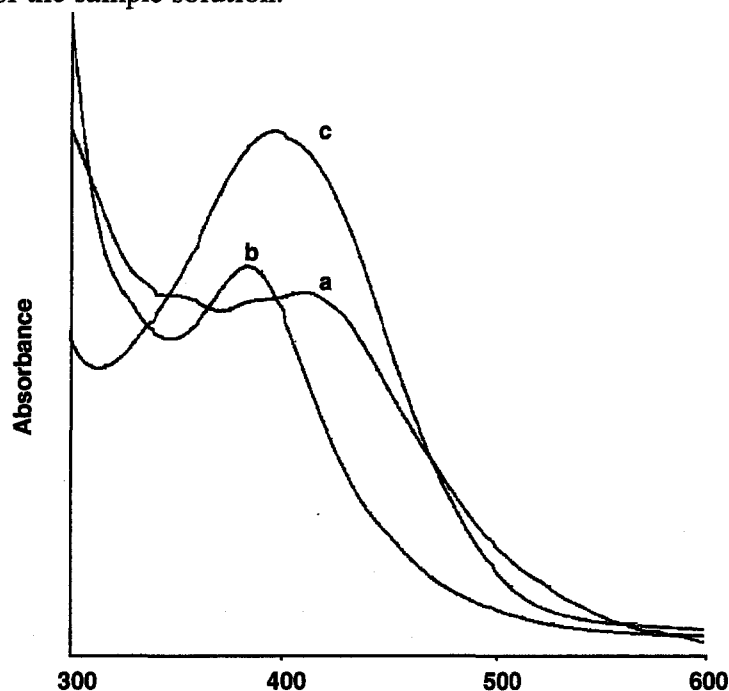
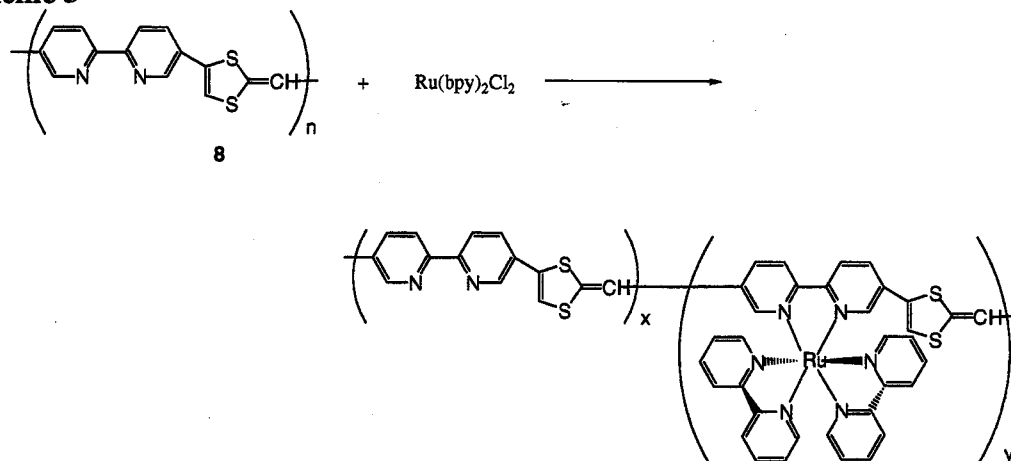


Figure 2. UV-vis absorptions of (a) **8**, (b) **9**, and (c) **10** in DMSO.

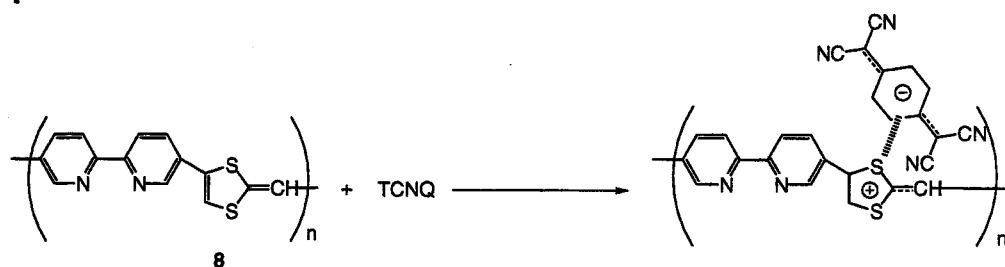
Scheme 3 outlines the synthesis of the polymer-ruthenium complex. Treatment of **8** with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{12}$ in heated water to give the product. The obtained complex, after repeated wash with water, was partially soluble in DMSO and DMF. The incorporation molar ratio of the metal into the repeating unit of **8** was 29 %, determined by the elemental analysis. The low incorporation ratio of the ruthenium into the polymer should be arisen from a steric hindrance of the ruthenium complex. A metal-to-ligand charge transfer (MLCT) transition of a low molecular weight complex $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, was located at 453 nm in DMSO. The UV-vis spectrum of the DMSO soluble part of the **8**-ruthenium complex exhibited a broad absorption due to the MLCT transition, which overlapped with that of π - π^* transition of **8** in the visible range. Quantitative analysis of the MLCT absorption of Ru complex also supported the Ru content. Figure 1b and 1e shows cyclic voltammograms of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. The redox peaks of $[\text{Ru}(\text{bpy})_3]^{2+}$ related to the metal center, changing the valence number from -I to III, were observed in the voltammograms.^{1h,13} The CV curves of the **8**-ruthenium complex showed both redox peaks (Figure 1c and f) for the $[\text{Ru}(\text{bpy})_3]^{2+}$ moiety and the dithiafulvene. The broad peaks corresponding to the ruthenium complex of **8**, in contrast to the peaks of the low molecular complex (Figure 1b and e), suggested the electronic interactions between the ruthenium units through the π -conjugated chain.^{1h}

Scheme 3



Similarly to the previous π -conjugated poly(dithiafulvene)s, **8** formed CT complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in DMSO. Although the dithiafulvene moiety was attached with the π -deficient bipyridyl unit and consequently showed the low electron donating property, **8** interacted with TCNQ as well as the benzene analogue **10**. This resulted from the structural preference of the dithiafulvene moiety for TCNQ. The obtained polymer CT complex was soluble in DMSO, DMF, acetonitrile and acetone, and partially soluble in THF. The ^1H NMR spectrum after an addition of TCNQ to the DMSO- d_6 solution of **8** showed a broad peak around aromatic region. The reason for these broad signals might be due to the complex having paramagnetic species.^{5c-e} The UV-vis absorption of the CT complex in DMSO exhibited peaks at 845, 762, 745 nm and large peak at 397 nm, indicating anion radical of TCNQ and partially charge transferred TCNQ, respectively, in the complex.⁵

Scheme 4



The electrical conductivities of these materials were investigated at room temperature by conventional two-probe technique. The polymer **8** exhibited an electrical conductivity of 3.1×10^{-4} S/cm. The high intrinsic conductivity of **8** achieved in this sample was due to the effective CT interaction between the dithiafulvene and the bipyridyl units in the π -conjugated framework. Similar high conductivity was observed in the dithiafulvene-pyridine system, previously. The **8**-ruthenium complex had a conductivity of 1.1×10^{-6} S/cm, two orders of magnitude lower than that of the uncomplexed polymer **8**. The conductivity of the polymer CT complex with TCNQ was 1.9×10^{-4} S/cm, not improved compared with the undoped polymer. These results suggest that steric hindrances of the complex moiety might decrease the intramolecular electron hopping.

Summary

In conclusion, the author has synthesized the π -conjugated polymer with the electron donating dithiafulvene unit and the electron accepting bipyridyl unit by cycloaddition polymerization of aldothioketene. UV-vis and CV measurement of the polymer indicated the effective donor-acceptor pair between the units. The polymer **8** formed the transition metal complex with ruthenium in water and the complex showed the hybrid redox system between the dithiafulvene and the tris(bipyridyl) ruthenium complex. The intrinsic conductivity of **8** was unexpectedly high due to the CT interaction between the units, which was comparable with that of the CT formation of **8** with TCNQ. The high intrinsic conductivity of **8**, which acted as a semiconducting material without doping, is notable.

Experimental Section

Materials. Unless otherwise noted, the materials were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium benzophenone ketyl and CaH_2 , respectively, and were stored under nitrogen before use. 5,5'-Diethynyl-2,2'-bipyridine (**7**) was prepared according to the literatures.⁶⁻¹⁰ $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ was synthesized according to the literature.¹²

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. IR spectrum was recorded on a Perkin Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography was carried out on TSK gel a-3000 by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. For cyclic voltammetry studies, thin polymer films (thickness, 10-20 nm) were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum before measurements. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were employed. Due to limitation of potential windows, $[\text{NET}_4]\text{BF}_4$ and $[\text{N}(\text{n-C}_4\text{H}_9)_4]\text{Br}$ were used as supporting electrolytes in anodic and cathodic scans, respectively. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 source meter. The polymer film was prepared by dropping of a DMSO solution onto glass plates equipped with platinum electrodes, followed by drying *in vacuo*.

Polymerization. To a solution of 5,5'-diethynyl-2,2'-bipyridine (**7**) (102 mg, 0.50 mmol) in THF (5 mL), 1.6 M solution of n-butyllithium in hexane (0.63 mL, 1.00 mmol) was added at 0 °C. After stirring for 0.5 h, the powder of sulfur (62 mg, 1.00 mmol) was added to the mixture. The reaction mixture was stirred for 2 h, then cooled at -55 °C and water (18 mg, 1.00 mmol) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.2 mL) and stirred for 0.5 h. The mixture was then poured into a large quantity of Et_2O . The obtained precipitate was washed with water to remove lithium salts. After drying *in vacuo*, a brown-colored polymer **8** was obtained (121 mg, 88 %). IR (KBr) 1575, 1558 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 1.1-1.8 (CH_2 of piperidine unit), 3.7 (N- CH_2 of piperidine unit), 4.3 (N- CH_2 of piperidine unit and $\text{CH}_2\text{C}(=\text{S})\text{N}<$), 6.8 (dithiafulvene), 7.4 (dithiafulvene), 7.7-8.0 (pyridine), 8.1-8.9 (pyridine); Anal. Calcd: C, 63.1; H, 3.6; N, 10.8; S, 22.4. Found: C, 64.0; H, 3.9; N, 9.9; S, 22.2.

CT Complex of 8 with TCNQ. An excess amount of TCNQ against repeating unit of **8** was added to the solution of **2** in DMSO, and the mixture was stirred for 15 min. The solution gradually became dark green. After the unreacted TCNQ was filtered off, the solvent was evaporated to obtain a dark green powder.

Transition Metal Complex with Ru(II). The mixture of **8** (45 mg) and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (73 mg) in water (3 ml) was heated under reflux for 24 h. After filtration of the mixture, water-soluble materials were removed by repeated wash with water to give the polymer complex (51 mg).

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Chapter 8

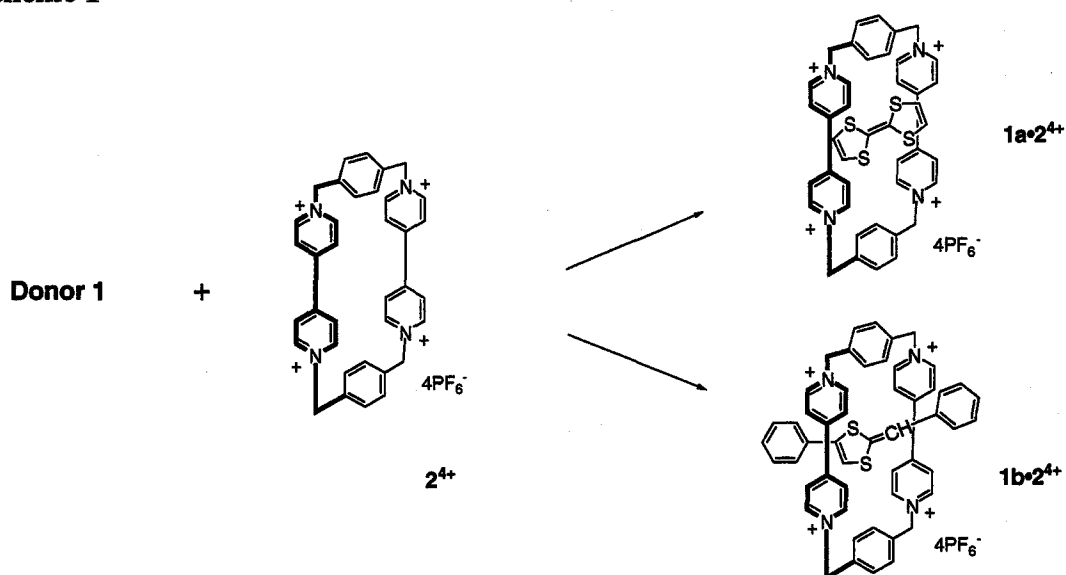
Self-Complexation of π -Conjugated Poly(dithiafulvene)s with Cyclic Acceptor to Form Pseudopolyrotaxane

Abstract: Mixing of 2-benzylidene-4-phenyl-1,3-dithiole (**1b**) and cyclobis(paraquat-*p*-phenylene) (**2**) as a cyclic acceptor in DMSO produced a green-brown solution, which showed a charge-transfer (CT) absorption band with a peak at 616 nm. The ^1H NMR spectrum of **1b**, after adding **2** in $\text{DMSO-}d_6$, showed upfield shifts of the peaks for the dithiafulvene moiety. These facts indicated that an insertion of **1b** into the cyclic acceptor by CT interaction led to the formation of a pseudorotaxane. Self-assembly of π -conjugated dithiafulvene polymers (**3**) and **2** by CT interaction gave pseudopolyrotaxanes in DMSO. The UV-vis and ^1H NMR spectra of the pseudopolyrotaxanes suggest that the incorporation ratio of the cyclic acceptors into the polymers depended on the molecular weights of **3**. The polymers with lower molecular weights seem to be more favorable for the polyrotaxane formation. After self-complexation of the polymer **3** with **2**, anodic shift of the oxidation potential of the dithiafulvene unit of **3** was observed in the cyclic voltammogram. In addition, the effective CT interaction between the dithiafulvene unit of **3** and the cyclic acceptor **2** afforded a high conductivity of the pseudopolyrotaxane.

Introduction

Rotaxanes are the molecules constructed by interlocked parts in the shape of one or more wheels that are trapped mechanically on the axle.¹ Recently, many these interlocked compounds have been prepared efficiently as consequence of the development of synthetic methods.² On the other hand, π -conjugated polymers have attracted great interest and a large number of papers about chemical and physical properties of these compounds have been published so far.³ Nevertheless, the studies focused on the hybrid systems between rotaxanes and π -conjugated polymers have been very limited.⁴ The integration of these chemistry could open up new areas of unique and desirable materials, e.g. sensors, switches, molecular devices and wires.^{4a,b,d}

Scheme 1



The good π -electron donor tetrathiafulvalene (TTF, **1a**) enters the cavity of the cyclic acceptor, cyclobis(paraquat-*p*-phenylene) (**2**), to form a strong complex in a pseudorotaxane manner by charge-transfer (CT) interaction.⁵ By use of this system in the self-assembly, a number of interlocked and intertwined compounds comprising TTF macrocycles and the cyclic acceptor **2** have been prepared.⁶ Controllable molecular shuttles and switches based on **1a** and **2** by external stimuli were also reported.^{5b,6e-g} The author has synthesized π -conjugated polymers with electron-donating dithiafulvene unit, which is a component of TTF, in the main chain.⁷ The poly(dithiafulvene)s could form CT complexes with organic acceptors such as 7, 7, 8, 8- tetracyanoquinodimethane (TCNQ).^{7a,c,d} It is hence possible to create self-assembling systems between the poly(dithiafulvene)s and various organic acceptors by CT interaction. In this chapter, the author describes a self-complexation of the π -conjugated poly(dithiafulvene) with **2**•4PF₆ by CT interaction. No π -conjugated polymer has ever consisted of a polyrotaxane formation by CT interaction. The construction of superstructures, such as catenanes, rotaxanes, double helices and knots, by CT interaction should offer the optical, magnetic, electric and enhanced conducting properties.

Results and Discussion

2-Benzylidene-4-phenyl-1,3-dithiole^{7a,b}(**1b**) was used as a model compound for the π -conjugated poly(dithiafulvene). Admixture of equimolar proportion of **2**•4PF₆ and **1b** in DMSO-*d*₆ produced instantaneously a green colored solution, which is diagnostic of charge-transfer complexation between the two components (Scheme 1). The ¹H NMR spectrum of this sample showed obvious changes in chemical shifts relative to those for free **1b** and **2**•4PF₆. The signals for the dithiafulvene protons moved significantly upfield and small shifts of peaks for **2** were observed (Table 1). In addition, the peaks due to the free **1b** and **2**•4PF₆ did not appear in this spectrum. These patterns of the chemical shift change indicated that the electron donor **1b** was inserted into the cavity of **2** creating a 1 : 1 complex as a pseudorotaxane form.^{5a} Addition of methyl viologen to the DMSO-*d*₆ solution of **1b** did not affect the chemical shift of **1b**. This result indicated that **1b** did not interact with the exterior of **2**. The complex [**1b**•**2**][PF₆]₄ in DMSO showed a charge-transfer absorption band centered at 616 nm in the UV-vis measurement (Figure 1). Spectrophotometric dilution analysis⁸ was performed on the solution at this wavelength at 25 °C yielded an association constant $K_a = 51 \text{ M}^{-1}$. The obtained value was lower than that of [TTF(**1a**)•**2**][PF₆]₄ ($K_a = 2600 \text{ M}^{-1}$ in acetone at 21 °C^{5c}) due to the weaker electron donating ability of **1b** than that of **1a**.^{5d}

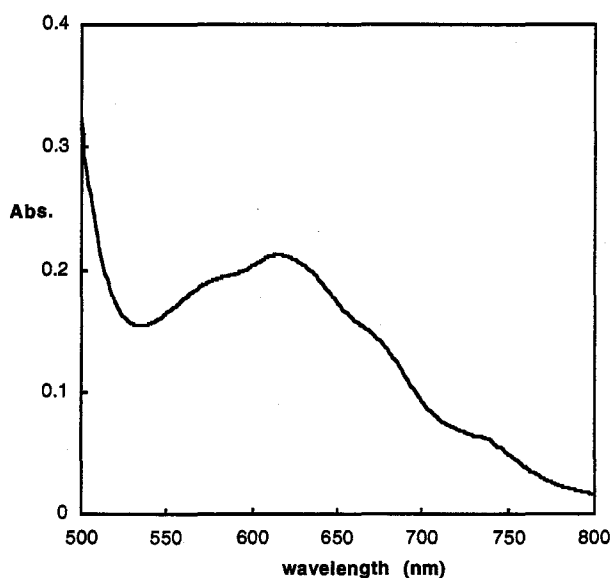


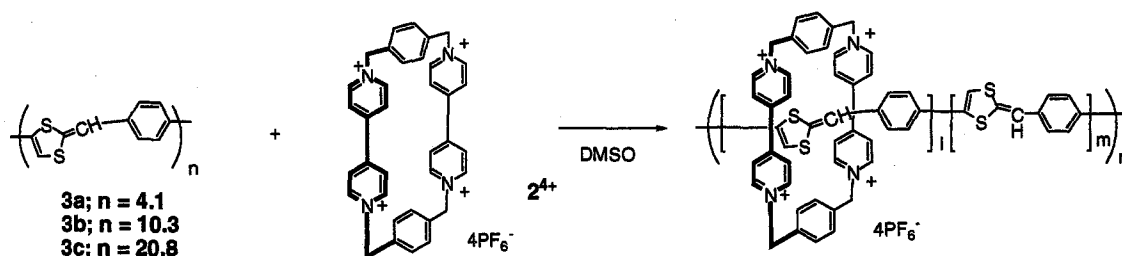
Figure 1. UV-vis absorption of a pseudorotaxane [**1b**•**2**][PF₆]₄ ($2.0 \times 10^{-5} \text{ M}$) in DMSO.

Table 1. The chemical shift of ^1H NMR for **1b**, **2⁴⁺** and **[1b•2][PF₆]₄** in DMSO-*d*₆ at ambient temperature^a

compound	benzylidene	dithiole	bipyridyl	bipyridyl	C ₆ H ₄	+NCH ₂
1b	6.79	7.20	-	-	-	-
2•4PF₆	-	-	9.42	8.63	7.69	5.80
[1b•2][PF₆]₄	6.47 (-0.32)	7.03 (-0.17)	9.44 (+0.02)	8.57 (-0.06)	7.76 (-0.07)	5.81 (+0.01)

^a The $\Delta\delta$ values calculated using the equation, $\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$, were indicated in parentheses.

Scheme 2



The π -conjugated poly(dithiafulvene)s **3** were synthesized by cycloaddition polymerization of aldothioketene derived from diethynylbenzene.^{7a,b} After polymerizations were finished, terminal thioketenes were quenched by addition of piperidine. Three kinds of polymers **3** having different degrees of polymerization (D.P.) were prepared by changing the polymerization times. In the ^1H NMR spectra of **3**, a broad peak for the benzylidene proton in the repeating dithiafulvene unit appeared at 6.7 ppm, as well as two broad signals at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. The D.P. for **3** employed in this system were **3a**; n = 4.2, **3b**; n = 10.3 and **3c**; n = 20.8, respectively, determined by the comparisons of the peak intensities in their ^1H NMR spectroscopies.⁷ The author investigated the self-assembly of the cyclic acceptor **2** and **3** (Scheme 2). After an excess of **2•4PF₆** was added to the DMSO-*d*₆ solution of **3**, an immediate formation of a green solution was observed, similar to the admixture of **1b** and **2•4PF₆**. The UV-vis spectrum of the resulting solution showed CT absorption bands ($\lambda_{\text{max}} = 614$ nm).

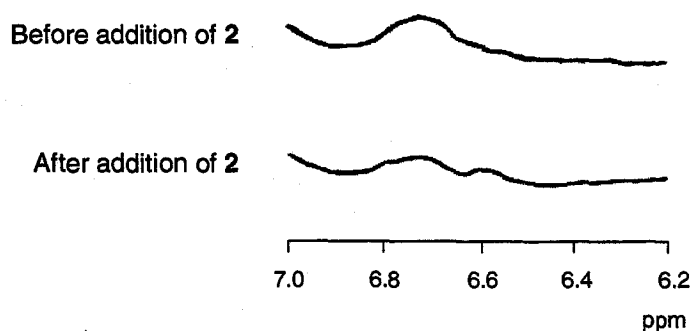


Figure 2. Partial ^1H NMR spectra of **3b** in DMSO-*d*₆ before and after adding **2**.

In the ^1H NMR spectrum of the same solution, a signal for the benzylidene proton was partially upfield-shifted, and a new broad peak for the benzylidene proton due to the

dithiafulvene unit complexed with **2** appeared at 6.6 ppm (Figure 2). The peak for the benzylidene proton of the free dithiafulvene moiety remained at 6.7 ppm. These facts indicated a pseudopolyrotaxane formation by the self-assembly of **3** and the cyclic acceptor **2** by CT interaction.

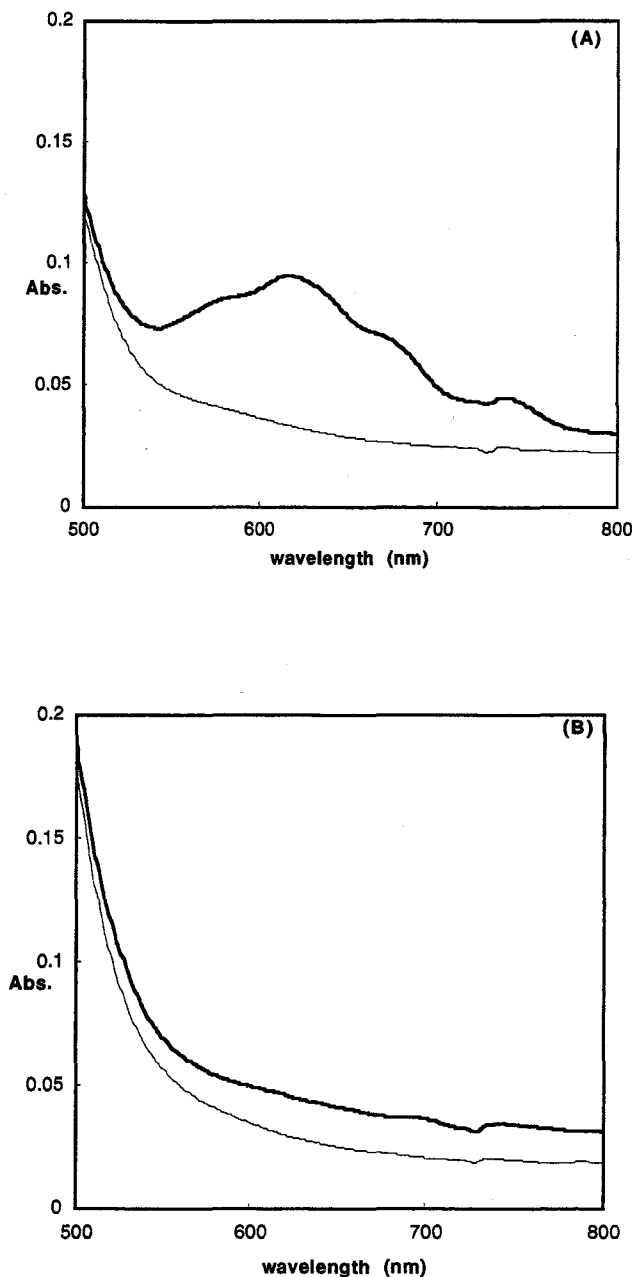


Figure 3. (A) UV-vis absorptions of **3a** (1.1×10^{-4} M of the dithiafulvene unit, solid line) and **3a** after addition of 10 fold excess amount of **2** against the dithiafulvene unit of **3a** (bold line) in DMSO. (B) UV-vis absorptions of **3c** (1.3×10^{-4} M of the dithiafulvene unit, solid line) and **3c** after addition of 10 fold excess amount of **2** against the dithiafulvene unit of **3c** (bold line) in DMSO.

The UV-vis absorption study demonstrated that the formation of the pseudopolyrotaxane was strongly affected by the molecular weight of **3**. Figure 3A shows the absorptions of the polydithiafulvene **3a** with the lowest molecular weight before and after addition of the acceptor **2** in DMSO. The characteristic of the CT absorption band between the dithiafulvene units and **2** appeared clearly after adding **2**. However, a DMSO solution of **2** and the polymer **3c** showed a vague CT absorption under the same condition to **3a** (Figure 3B). This result suggested that incorporation ratios of the acceptor **2** depended on the molecular weights of **3**. The polymers **3** with the lower molecular weights seem to be more favorable for the complex formation. A high concentrated solution of **2** and **3c** in DMSO showed a distinct CT absorption.

^1H NMR was also employed for estimations of the incorporation ratios of **2**. For this study, the cyclic acceptor **2** (2 mg) and **3** (1 mg) were mixed in DMSO- d_6 (0.5 ml), then the resultant solution was examined by ^1H NMR. Two broad peaks for the benzylidene proton originated from the free and complexed dithiafulvene units were observed as above mentioned. Comparisons of their peak areas suggests that the incorporation ratios of **2** in the dithiafulvene moiety of **3a**, **3b** and **3c** were found to be 34, 31 and 16 %, respectively (aberrations are ± 6 %). This fact also suggested that the incorporation ratio of **2** depends on the molecular weight of **3** and the low molecular weight polymers are preferable for the rotaxane formation. The easy 'threading' of **3a** and **3b** resulted from their higher proportion of terminal units compared with **3c**.

After the mixtures of **2** and **3** in DMSO were left for a few minutes, the intensities of the CT absorptions decreased gradually and green precipitates were deposited. The precipitates were characterized by IR and elemental analysis. IR spectra of the obtained precipitates showed a peak for the dithiafulvene unit in **3** at 1575 cm^{-1} as well as a peak for bipyridinium moiety of **2** at 1634 cm^{-1} , suggesting that the precipitates were composed of **2** and **3** as rotaxane manners. Elemental analysis of the precipitates revealed that 24-29 % of the repeating dithiafulvene units complexed with **2**. This value was independent of the molecular weight of **3**.

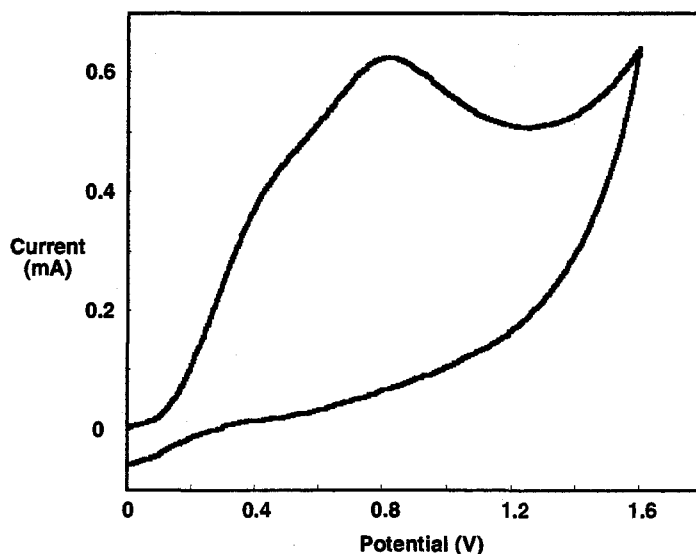


Figure 4. Cyclic voltammogram of **3b** after the 20 % incorporation of **2** against the dithiafulvene unit.

The pseudopolyrotaxane consisted of **2** and **3b** in the ratio of **2** to the dithiafulvene unit of **3b** = 2 : 10 was prepared by accurate addition of **2** into the polymer solution in DMSO and continuous evaporation. The redox property of the obtained pseudopolyrotaxane was examined by cyclic voltammetry (CV). In the cyclic voltammogram of the uncomplexed **3b**, an oxidation peak for the dithiafulvene unit appeared at 0.61 V vs. Ag/Ag⁺.^{7b} After complexation of **3b** with **2**, the oxidation peak moved to 0.83 V vs. Ag/Ag⁺ (Figure 4). The drastic shift of the oxidation potential for the pseudopolyrotaxane originated from the electron withdrawing character of **2**. A shoulder peak appeared at around 0.6 V results from the uncomplexed dithiafulvene moiety of **3b**. The electrical conductivity of the pseudopolyrotaxane was measured by the conventional two-probe technique. The pseudopolyrotaxane consisted of **2** and **3b** (dithiafulvene unit of **3b** : **2** = 10 : 2) had a conductivity of 7.6×10^{-4} S/cm, while the uncomplexed polymer **3b** exhibited an electrical conductivity of 3.4×10^{-7} S/cm under the same condition. Interestingly, the effective CT interaction between the dithiafulvene unit and the cyclic acceptor **2** afforded the highly improved conductivity of the pseudopolyrotaxane.

Summary

The author has demonstrated that the electron donating dithiafulvene was inserted into the cavity of the cyclic acceptor **2** creating a 1 : 1 complex as a pseudorotaxane formation and have created the first pseudopolyrotaxane consisted of the π -conjugated polymer and the macrocycle by CT interaction. The incorporation ratio of **2** in the polydithiafulvene **3** depended on the molecular weight of **3**. The self-complexation of the polymer **3** and **2** gave rise to the anodic shift of the oxidation potential and the high conductivity of **3**. This system, which is regarded as a semi-conducting pseudopolyrotaxane, will find an application in the macromolecular, supramolecular and material fields of chemistry.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. The solvents were dried and distilled under N₂. Synthesis of the dithiafulvene **1b** has been described in a previous paper.^{7b} Cyclobis(paraquat-*p*-phenylene) (**2**) was synthesized according to the literature.⁹

Measurements. ¹H NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. For the cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurements. Electrical conductivity was measured at room temperature by the two-probe technique using a Keithley 2400 source meter. The polymer films were prepared by dropping DMSO solutions onto glass plates equipped with platinum electrodes, followed by drying *in vacuo*.

Polymerization. π -Conjugated poly(dithiafulvene)s **3** were synthesized by cycloaddition polymerization.^{7b} The polymerization reactions were conducted for 0.5 h, 1 h and 3 h to prepare **3a**, **3b** and **3c**, respectively.

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Chapter 9

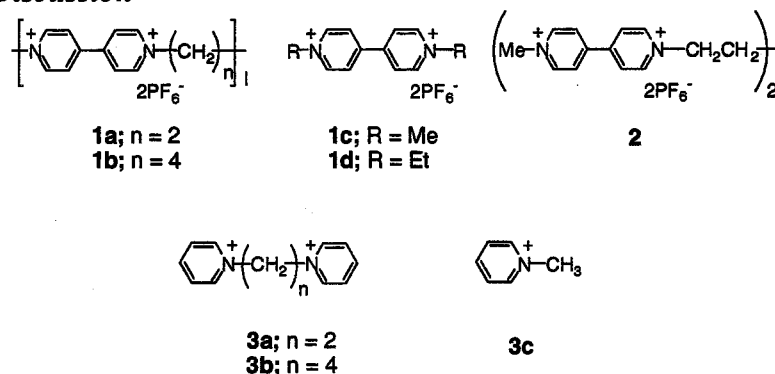
Conjugative Effect through Saturated Polymethylene Chain; Enhancement of $\sigma^*-\pi^*$ Conjugation by Intramolecular Charge-Transfer between Dithiafulvene and Pyridinium Unit

Abstract: New $\sigma-\pi$ conjugation system through saturated polymethylene chains were achieved. Polyviologens (**1**) showed small conjugative effects in their UV-vis measurements, which are increased with the decrease of the spacer polymethylene chain. *Ab initio* calculations, using the 6-31 G* method, provided that low lying LUMO resulted from an interaction between the σ^* of the polymethylene unit and π^* of the pyridinium moiety affords the conjugative effect. It was noteworthy that polymers **4** with an acceptor-donor-acceptor (pyridinium-dithiafulvene-pyridinium) moiety enhance the conjugation due to efficient electronic flows along the polymer chains in DMSO. Conformational changes of **4** in THF/DMSO mixed solvent caused interruptions of the conjugations, however, the polymer **4a** still showed the effective conjugation system owing to the rigid structure. The redox and conducting properties of **4** were also investigated. Both studies gave some implications of the conjugative effects of **4**.

Introduction

π -Conjugations are stable electronic states resulted from π -electron delocalizations throughout the polymeric chains with alternate saturated and unsaturated bonds. Many kinds of π -conjugated polymers have been synthesized and studied extensively for a past few decades to be utilized for advanced conducting and optical materials owing to their π -electron delocalization systems.¹ Electron delocalization between σ bonds and π systems (σ - π conjugation) has been developed in various disilyl compounds containing unsaturated or aromatic groups,² however, never been established in combinations of polymethylene chains and π -units. Exceptionally, substitution of an alkyl group on an aromatic compound leads to delocalization of σ -electrons into an adjacent π -bond, known as hyperconjugation.³ Here the author demonstrates that new electron delocalized σ - π systems between pyridinium π -units and saturated polymethylene chains are accomplished, and additional incorporation of an acceptor-donor-acceptor structure (pyridinium-dithiafulvene-pyridinium) into the π -units enhances the effects. It is known that intramolecular interaction between the electron sufficient dithiafulvene⁴ and the deficient pyridinium moieties gives rise to an efficient charge-transfer (CT).⁵

Results and Discussion



The author initially prepared and studied optical properties of viologen (bipyridinium) polymers (**1a,b**) with different methylene spacers.⁶ Figure 1 shows the UV absorption spectra of the polymers and methylviologen (**1c**) in CH_3CN . The absorption peaks due to π - π^* transition of the viologen units in polymer **1a** and **1b** were located at 269 and 264 nm, respectively, showing small but certain bathochromic shifts from that of **1c** ($\lambda_{max} = 259$ nm). Although the adjacent viologen units were tethered by non-conjugated polymethylene chains, the peaks of **1a** and **1b** were found to show gradual red-shifts as the methylene intervals became shorter. Ethylviologen (**1d**) shows an absorption peak at similar position ($\lambda_{max} = 258$ nm) to **1c**, indicating no effect of ethyl substitution on the UV absorption. A bisviologen compound (**2**) having ethylene spacer unit showed an absorption ($\lambda_{max} = 260$ nm) between those of **1a** and **1c**. These facts suggest some conjugative effects (C-C hyperconjugations) through saturated polymethylene chains in those viologen systems, which were enhanced with a decrease of the methylene length. Furue and Nozakura have also observed such red-shifts of absorptions for bisviologens with various polymethylene spacers, as their spacer lengths decreased.⁷ Interpolymer effects on the absorptions of **1a,b** were excluded, since those spectra were in accordance with Lambert-Beer law. Benzene analogues connected by

ethylene unit do not show such effects, indicating interruptions of π -conjugations by the saturated units in the benzene analogues.^{3c,8}

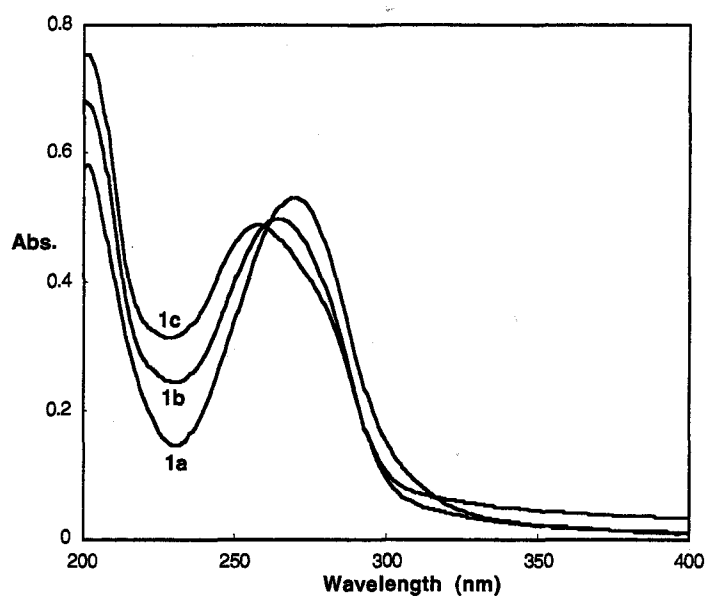


Figure 1. UV-vis spectra of (A) **1a**, **1b**, and **1c** in CH_3CN .

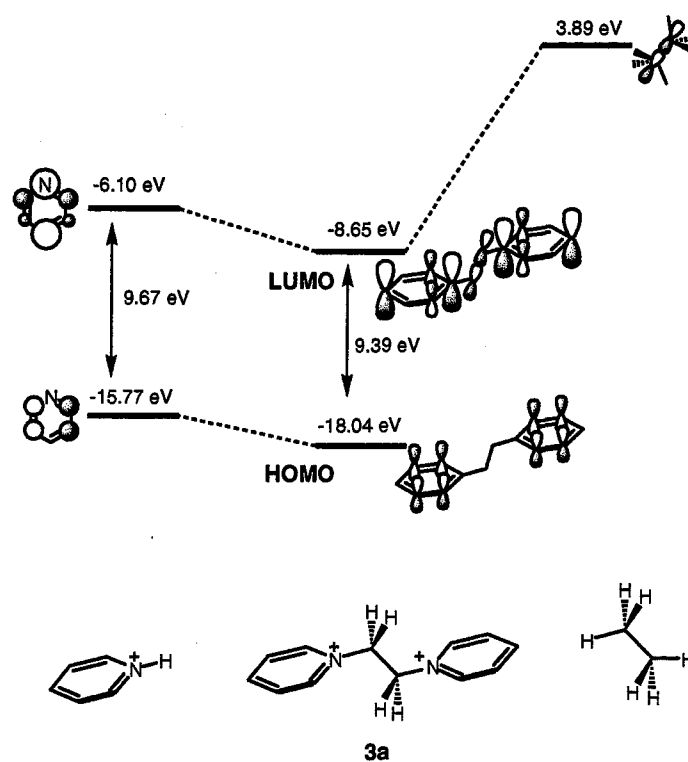
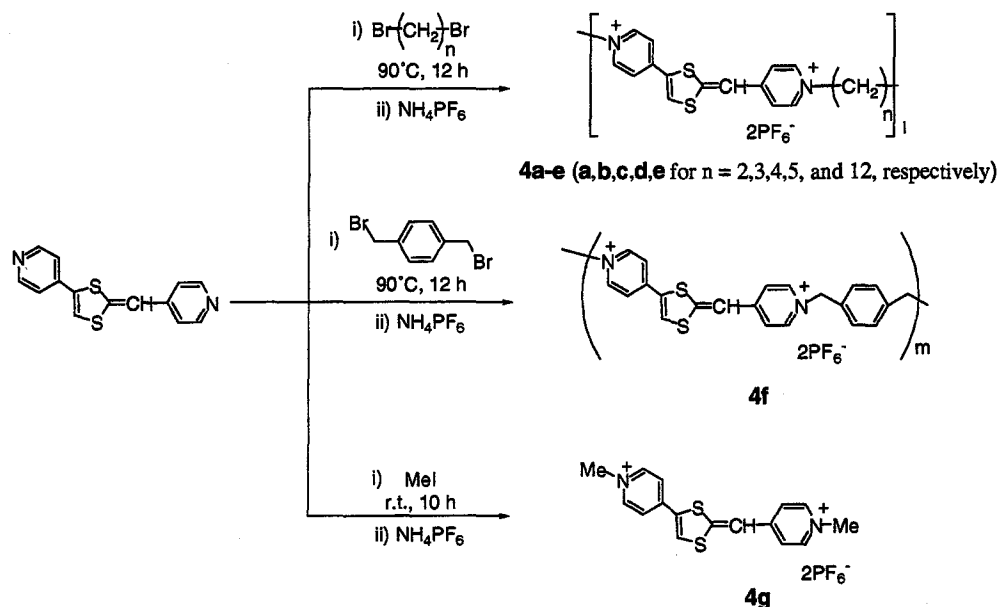


Figure 2. Orbital correlation diagram for **3a**, based on the PM3 calculations.

Calculation of HOMO and LUMO energies of 1,1'-(1,2-ethanediyl)bis(pyridinium) (**3a**) using the PM3 Hamiltonian was carried out to predict the conjugative effect for **1a**. Although a through-space interaction of the π system is possible in the syn conformation, the C_{2h} anti conformation was the optimized geometry for **3a**. In the anti conformation, the π systems are distant from one another and unlikely to couple through-space. Interaction of the π^* orbitals of two pyridinium rings through $C_{sp^3}-C_{sp^3}$ σ^* bond gives rise to an effective $\sigma^*-\pi^*$ conjugation, leading to reduce the orbital energy of the LUMO (Figure 2). No σ orbitals of the ethylene moiety appear in the HOMO level of **3a**. These results suggest that the bathochromic shift for **1a** is derived from its low-lying LUMO level due to the $\sigma^*-\pi^*$ conjugation. Additionally, *ab initio* calculation of 1,1'-(1,4-butanediyl)bis(pyridinium) (**3b**) also showed some formation of the $\sigma^*-\pi^*$ conjugation. The C-C hyperconjugation is developed by combination with electron-deficient π units due to a usual electron releasing property of the C-C bond.⁹

Scheme 1.



Scheme 1 provides the syntheses of a series of polymers **4a-f** with an acceptor-donor-acceptor (pyridinium-dithiafulvene-pyridinium) moiety in the π -unit from 2,6-bis(4-pyridyl)-1,4-dithiafulvene and dibromoalkanes after counterion exchanges. A low molecular weight compound **4g** as a model compound was also prepared by use of the dithiafulvene and iodomethane (Scheme 1). The structures of **4a-f** were confirmed spectroscopically in comparison with that of **4g**. In ^1H NMR spectra of the polymers **4a-f**, incidental small peaks to the main peaks were attributed to the polymer end groups. For example, ^1H NMR spectrum of **4d** (Figure 3, bottom) showed small peaks due to the terminal protons at 7.2, 7.6, 8.1 and 8.6 ppm, which appeared at slightly upfield compared with the main peaks of the corresponding repeating units. Judging from the peak intensities, the number-average molecular weights (M_n) of **4a-f** could be determined and found to be ranged from several thousands to twelve thousands.

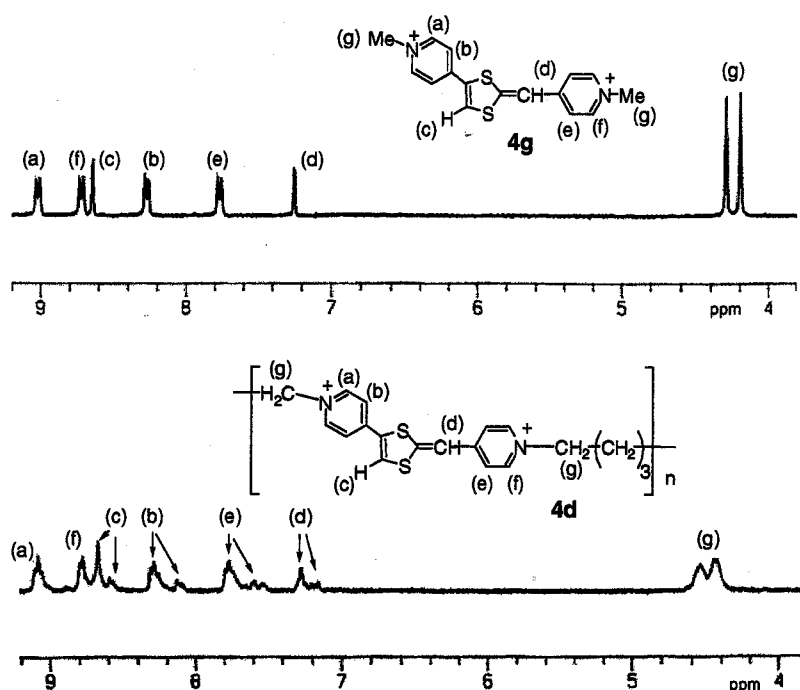


Figure 3. ^1H NMR spectra of **4g** (upper) and **4d** (bottom) in $\text{DMSO}-d_6$.

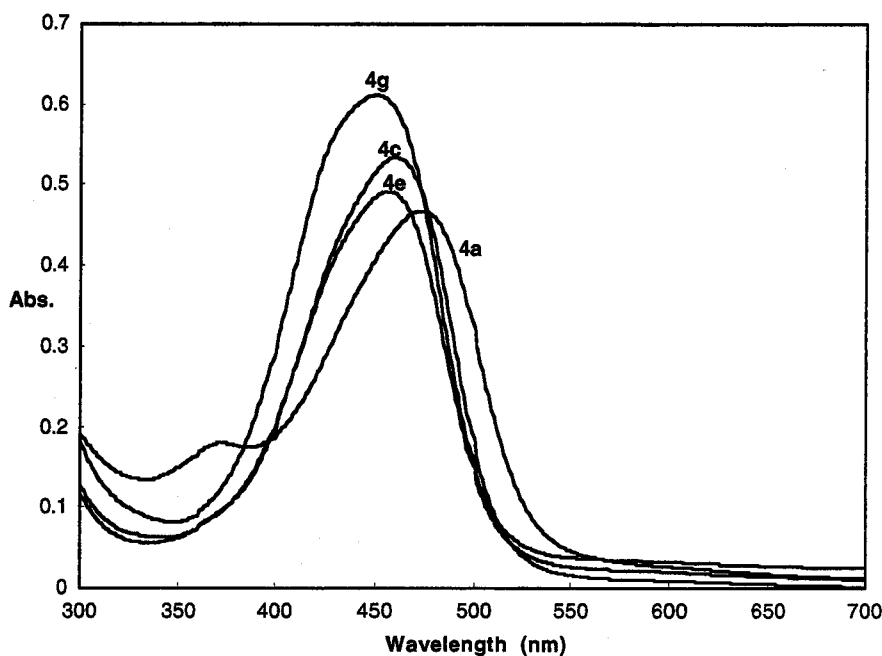
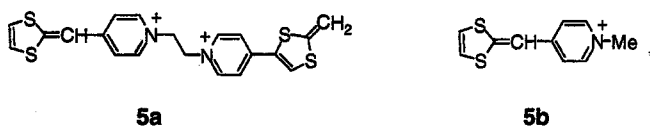


Figure 4. UV-vis spectra of **4a**, **4c**, **4e**, and **4g** in DMSO.

Similarly to the viologen systems, the absorptions of **4a-e** were located at longer wavelengths than that of **4g** and shifted gradually to longer wavelengths as the methylene spacer decreased (Figure 4 and Table 1). The polymer **4f** with a phenylene moiety in the spacer had an absorption maximum at 465 nm. The peak intensities of the absorptions in **3** were proportional to the concentrations of the sample solutions, showing effective conjugations between the π -units and the methylene chains in **4a-f**. The positions of the absorption edges of **4a** and **4g** (**4a**; 561 nm, **4g**; 522 nm) gave

respective band gaps as 2.21 and 2.38 eV. In the same way, the band gaps of **1a** and **1c** (band edge of **1a**; 325 nm, **1c**; 315 nm) are obtained as 3.82 and 3.94 eV from Figure 1, respectively. Comparison of the gap difference between **1a** and **1c** (= 0.12 eV) to that between **4a** and **4g** (= 0.17 eV) suggests that the electronic delocalization in **4a** is very efficient.



PM3 calculation of dithiafulvene-pyridinium compounds **5** showed that HOMO-LUMO band gaps of **5a** and **5b** were 5.15 and 5.95 eV, respectively. The gap difference between **4a** and **4b** is found to be 0.80 eV, which is larger than that between **3a** and **3c** (HOMO-LUMO gap difference = 0.25 eV) calculated by the same method. This result also supports the observed effective σ - π conjugation system of **4a** in the UV spectrum. The significant electronic delocalizations in **4a-f** may be owing to the intramolecular CT structure. The electron-donating dithiafulvene units increase electron densities of the adjacent pyridinium moieties by the CT interaction, which would effectively enhance the electronic flows along the polymer chains. To the best of the author's knowledge, these polymers, particularly **4a**, showed the first effective conjugation throughout saturated methylene chains in polymeric systems.

Table 1 UV-vis Results of 4

compounds	λ_{\max} in DMSO (nm)	λ_{\max} in THF/DMSO (98:2, nm)	$\Delta\lambda$ (nm) ^a
4a	473	471	24
4b	463	456	14
4c	461	449	12
4d	457	443	8
4e	455	446	6
4f	465	451	16
4g	449	448	-

^a $\Delta\lambda = \lambda_{\max}$ (polymers) in DMSO - λ_{\max} (**4g**) in DMSO.

The peaks of **4c-f** in THF/DMSO (98:2) mixed solvent became close to that of **4g**, in contrast, the absorption of **4a** in the mixed solvent was same as that in DMSO (Figure 5 and Table 1). Since the both λ_{\max} positions of **4g** in DMSO and in THF/DMSO are almost same, the peak shifts of **4c-f** in THF/DMSO should result from conformational changes of the polymers to interrupt the conjugations. The small peak difference in **4a** system indicates that the short ethylene chain between the units retains and restricts the polymer conformation of **4a**. The resultant rigid conformation of **4a** would also cause the effective σ^* - π^* conjugation.

In order to elucidate the redox properties of the dithiafulvene moieties in **4**, cyclic voltammetry measurements were carried out. The model compound (**4g**) showed a single oxidation peak at 0.95 V vs. Ag/Ag⁺ in CH₂Cl₂. The cast films of the polymers (**4a-f**) gave single-broad oxidation peaks between 1.5 and 1.6 V vs. Ag/Ag⁺ in CH₂Cl₂. Apparent anodic shifts of the oxidation potentials for the dithiafulvene unit in **4a-f** compared with that of **4g** indicated that the dithiafulvene units incorporated in the polymeric systems were stabilized against oxidation. Previous poly(dithiafulvene)s

which contain the dithiafulvene units in the π -conjugated main chains showed similar anodic shifts in their CV,^{4a,b} suggesting that the observed peak shifts in this work may be arisen from the σ - π conjugative effects of the polymers **4a-f**.

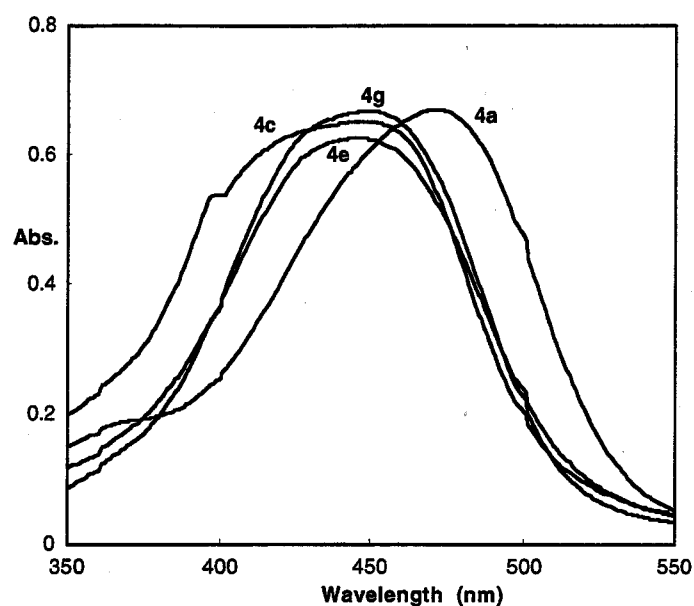


Figure 5. UV-vis spectra of **4a**, **4c**, **4e**, and **4g** in THF/DMSO (98 : 2).

The intrinsic electrical conductivities (unoxidized conductivities) of **4a**, **4c**, **4e**, and **4f** were measured by conventional two-probe technique and are summarized in Table 2. Even though they were not doped with any oxidant, the conductivities of them were relatively high because of the intramolecular CT units in the polymer structures. The increased conductivities with the decrease of the spacer units may imply a correlation between the conductivity and the σ - π conjugation.

Table 2 Conductivities of **4a**, **4c**, **4e**, and **4f**

polymer	conductivity (S/cm)
4a	1.5×10^{-4}
4c	5.4×10^{-5}
4e	4.7×10^{-6}
4f	2.9×10^{-4}

Summary

In summary, the author provided that precise molecular designs afforded new σ - π conjugative effects between the pyridinium π -units and the polymethylene chains. These results suggested that extensions of the hyperconjugations were achieved through saturated chains and enhanced by the incorporation of the intramolecular CT structure into the π -unit. This effect was controllable by systematic changes of the polymethylene spacer length. The examples presented here may have implications for other cases where observations of unusual electronic interactions have been made.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N₂.

Measurements. ¹H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Calculations for molecular orbitals were carried out by use of the Spartan Package; Wavefunction, Inc., Irvin, CA, USA. The orbital energies for **3** and **5** were evaluated after calculation of geometry optimization by PM3 semi-empirical molecular orbital method. For cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. The experiments were carried out in CH₂Cl₂ solution of the compounds containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Scan rate was 300 mV/s. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit. The polymer film was prepared by dropping of a DMF solution onto glass plates equipped with platinum electrodes, followed by drying at room temperature *in vacuo*.

2,6-Bis(4-pyridyl)-1,4-dithiafulvene. 4-(4-Pyridyl)-1,2,3-thiadiazole (2.44 g, 15 mmol) dissolved in dry CH₃CN (45 ml) was added NaH (60 mg, 60 % mineral oil dispersion, 15 mmol) and left overnight. The mixture was filtered to give 2,6-bis(4-pyridyl)-1,4-dithiafulvene as a yellow solid (1.61 g, 79 %). ¹H NMR (270 MHz, CDCl₃) δ 6.50 (s, 1H), 6.92 (s, 1H), 7.17 (d, 2H), 7.33 (d, 2H), 8.58 (d, 2H), 8.65 (d, 2H); Elemental analysis. Calcd: C, 62.19; H, 3.73; N, 10.36; S, 23.72. Found: C, 61.66; H, 3.87; N, 10.51; S, 23.38.

Polymerization. General procedure for the polymerization of **4a-f** is as follows. Dibromoalkanes (0.50 mmol) and 2,6-bis(4-pyridyl)-1,4-dithiafulvene (138 mg, 0.51 mmol) were dissolved in DMF (4 ml). The mixture was agitated with heating at 90 °C for 12 h. The resultant precipitate was collected and suspended in water. A saturated aqueous solution of NH₄PF₆ was added to the suspension until no further precipitation was observed. After filtration, the precipitate was washed with water and dried.

4a: 61 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 5.0, 5.1, 7.3, 7.7, 8.3, 8.6, 8.7, 9.0; *M*_n = 3350. **4b:** 74 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 2.6, 4.6, 4.7, 7.3, 7.8, 8.3, 8.6, 8.8, 9.1; *M*_n = 5450. **4c:** 77 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 2.0, 4.5, 4.6, 7.3, 7.8, 8.3, 8.7, 8.8, 9.1; *M*_n = 7610. **4d:** 79 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 1.4, 1.9, 4.4, 4.5, 7.3, 7.8, 8.3, 8.7, 8.8, 9.1; *M*_n = 9160. **4e:** 58 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 1.3, 1.9, 4.4, 4.5, 7.3, 7.7, 8.3, 8.7, 8.8, 9.1; *M*_n = 12150. **4f:** 82 % yield; ¹H NMR (270 MHz, DMSO-*d*₆) δ 5.7, 5.8, 7.3, 7.6, 7.8, 8.3, 8.7, 8.9, 9.2; *M*_n = 4520.

Model compound (4g). Methyl iodide (1.71 g, 12 mmol) and 2,6-bis(4-pyridyl)-1,4-dithiafulvene (135 mg, 0.50 mmol) were dissolved in DMF (4 ml). The mixture was stirred at room temperature for 10 h. The resultant precipitate was collected and suspended in water. A saturated aqueous solution of NH₄PF₆ was added to the suspension until no precipitation was observed. The precipitate was washed with water (202 mg, 68 %). ¹H NMR (270 MHz, DMSO-*d*₆) δ 4.20 (s, 3H), 4.30 (s, 3H), 7.26 (s, 1H), 7.77 (d, 2H), 8.28 (d, 2H), 8.65 (s, 1H), 8.72 (d, 2H), 9.02 (d, 2H); Elemental analysis. Calcd: C, 32.55; H, 2.73; N, 4.75. Found: C, 32.78; H, 2.70; N, 4.79.

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Part III

Preparation of Conjugated Poly(thioketene dimer)s

Chapter 10

Synthesis of π -Conjugated Poly(thioketene dimer)s and Their Electron Donating Properties

Abstract: New π -conjugated polymers (**2**) with the thioketene dimer unit were prepared by cycloaddition polymerization of bithioketene derived from bis(triphenylphosphonium chloride) (**1**). The structures of the polymers were compared with that of 2,4-dibenzylidene-1,3-dithietane (**3**), which was prepared by dimerization of phenylthioketene derived from benzyltriphenylphosphonium chloride, by use of IR and ^1H NMR. The lower energy absorption edges of **2** were located at longer wavelengths than that of the model compound **3**, due to developments of π -conjugations in **2**. The cyclic voltammogram of **3** showed irreversible two-step oxidation peaks at 0.25 and 0.61 V vs. Ag/Ag^+ , indicating that the electron donating ability of **3** is stronger than that of tetrathiafulvalene (TTF). The electron donating properties of the polymers **2** were also confirmed by cyclic voltammetry and were found to depend on aromatic structures in **2**. The polymer **2** formed charge-transfer (CT) complexes with TCNQ (1:1 ratio of the repeating unit in **2** to TCNQ) in DMSO. The degrees of CT in the complex were investigated by UV and IR measurements. In the solid state, the complex of **2b** contained partially charge-transferred TCNQ (degree of CT = 0.59), resulting in higher conductivity than that of **2a**.

Introduction

Thioketenes are important and highly reactive intermediates. The reactivity of thioketenes shows features of the analogous ketene chemistry and has been extensively studied for a long time.¹ Recently, thioketene chemistry has noticeably grown in the field of the coordination of transition metals² and metabolism³. It has been suggested that thioketenes are potential biological reactive intermediates and induce DNA strand breaks.⁴

Thioketenes readily reacted with protic nucleophiles to give thiocarboxylic acid derivatives⁵ or undergo cycloadditions across the C=C bond.⁶ In addition to the ketene-type chemistry, the presence of sulfur atom allows thioketene reactions reminiscent of thiocarbonyl congeners; typical examples are the formation of *S*-oxides,⁷ thiophilic attack of organometallics⁸ or cycloadditions across the C=S bond.^{6a,9} The most common example of (2+2) cycloadditions between thioketenes and C=S compounds is a dimerization of thioketenes to give 2,4-bis(alkylidene)-1,3-dithietanes.^{6a,10} Such dimers have been known for more than 100 years and synthesized by various methods.

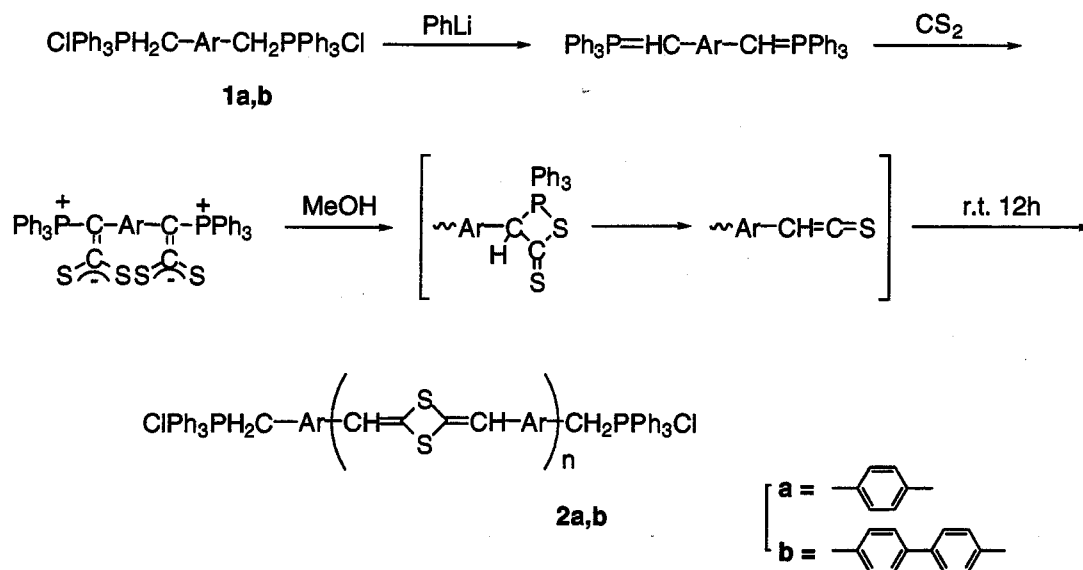
There is a long-standing interest in the chemistry and properties of cyclic compounds containing sulfur atom in modern material chemistry due to their redox chemistry. Especially, the focus has been on dithiole derivatives, e.g. dithiafulvenes and tetrathiafulvalenes,¹¹ since the finding of metallic conductivity¹² and low temperature superconductivity¹³ in radical cation salts. The quite low oxidation potentials of 1,4-dithiin compounds have been reported, recently.¹⁴ Therefore, the potential electronic property of the thioketene dimer moiety is considerably attractive with the aim of application to a new and better π -donor. Even though these dimer compounds have been characterized spectroscopically, no physical investigation including electric and magnetic properties of the thioketene dimers has been reported up to date.

From a viewpoint of polymerizations, the direct use of thioketenes in polymer synthesis has been very limited,^{6a,15} although ketenes have been employed in many kinds of polymerizations.¹⁶ In the previous chapters, the author has developed polymer syntheses by use of a cycloaddition reaction between an aldothioketene and its alkynethiol tautomer affording an electron donating dithiafulvene moiety.¹⁷ In this chapter, the author describes the synthesis, optical properties, and electrochemical analysis of π -conjugated polymers having electron-donating thioketene dimer units in the main chain.¹⁸ Formations of charge-transfer (CT) complexes of the polymers with tetracyanoquinodimethane (TCNQ) were also studied.

Results and Discussion

The π -conjugated poly(thioketene dimer)s were prepared by the cycloaddition polymerization of bistihioketenes derived from bis(triphenylphosphonium salts) (**1**). Treatment of **1** with phenyllithium and carbon disulfide in Et₂O generated bisbetaines. The resulting mixture was poured into a large amount of MeOH to afford the bistihioketenes and left for 12 h to effect polymerization. An insufficient amount of MeOH led to a recovery of the monomer, suggesting that this reaction was much affected by the polarity of the reaction medium. The polymers **2** were obtained as yellow precipitates and soluble in DMF and DMSO. The molecular weight measurement of **2a** as a representative polymer was performed by GPC in eluent DMF with polystyrene standards. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were 10280 and 2690, respectively. The molecular weight distribution (M_w/M_n) of the polymer was 3.82.

Scheme 1



The structures of **2** were confirmed by IR and ^1H NMR spectroscopies, compared with those of 2,4-dibenzylidene-1,3-dithietane (**3**) as a model compound. A model dimerization of phenylthioketene derived from benzyltriphenylphosphonium chloride gave **3** in a high yield.^{10c} The IR spectrum of **3** showed a peak at 1652 cm^{-1} due to a C=C vibration of the ylide unit. The polymer **2a**, for example, had the same peak at 1653 cm^{-1} in the spectrum, suggesting the thioketene dimer unit in the polymer. In the ^1H NMR spectrum of **2a** (Figure 1), a broad peak for the benzylidene proton in the repeating unit appeared from 7.1 to 7.5 ppm. The spectrum also showed a peak due to the terminal benzyl protons at 5.1 ppm. Therefore, it is possible to compare the peak intensities of the repeating unit with that of terminal moiety in order to estimate the degree of polymerization (D.P.) of the polymer **2**. The D.P. values of **2a** and **2b** were determined as 8.3 ($M_n=2290$) and 7.1 ($M_n=2700$), respectively. These results are consistent with the values from GPC data.

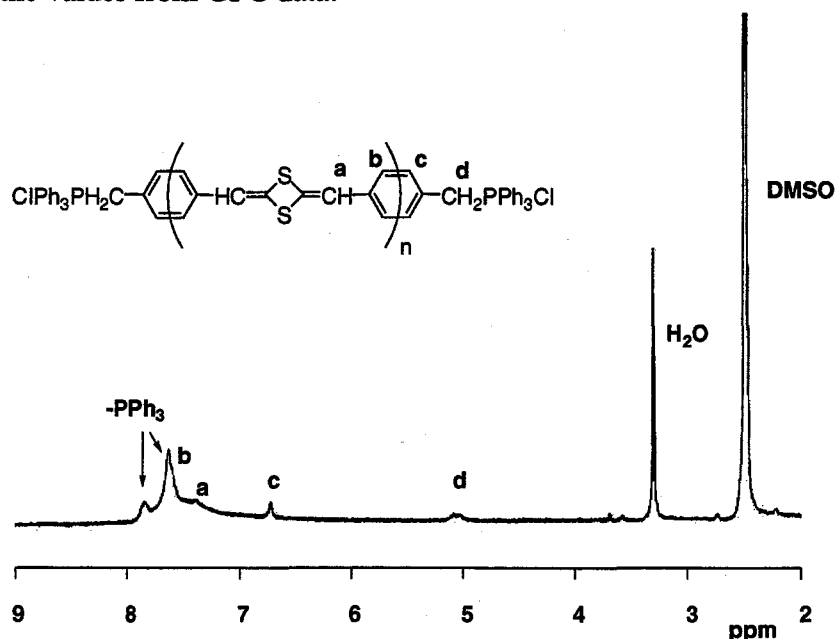


Figure 1. ^1H NMR spectrum of **2a** in $\text{DMSO}-d_6$.



Figure 2 shows UV-vis absorption spectra of the thioketene dimers. The model compound **3** had an absorption maximum due to the π - π^* transition at 364 nm in CH_3CN . The spectrum of **2a** in the same solvent exhibited no absorption maximum, however, was tailing beyond 550 nm. The lower energy absorption edge of **2a** was largely bathochromic shifted in comparison with that of the model compound **3**, which was located around 420 nm. This red-shift indicated an effective expansion of the π -conjugation system in **2a**. The smaller bathochromic shift of **2b** than that of **2a** was due to a steric distortion of the biphenyl moiety.

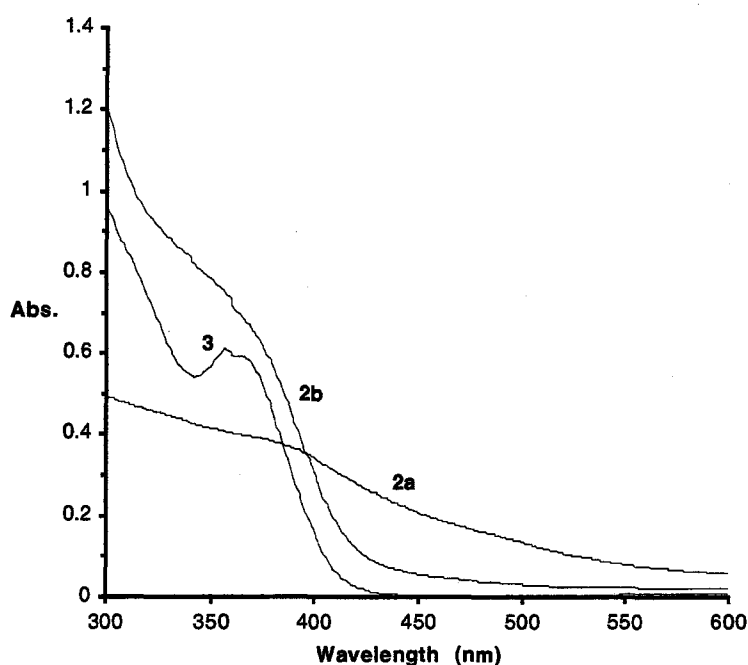


Figure 2. UV-vis absorption spectra of **2a**, **2b**, and **3** in CH_3CN .

Cyclic voltammetry was performed in order to elucidate the electric property of the thioketene dimer **3**. The cyclic voltammogram of **3** showed irreversible two-step oxidation peaks at 0.25 and 0.61 V vs. Ag/Ag^+ (Figure 3A). The first oxidation potential of **3** is remarkably lower than those of 2,6-bisphenyl-1,4-dithiafulvene (**4**)^{8b} ($E_{\text{pa}} = 0.40$ V) and TTF ($E_{\text{pa}} = 0.39$ V), indicating that **3** acts as a stronger electron donor than the dithiafulvene and TTF. As shown in Figure 3B, the cast film of **2a** gave two-step broad oxidation peaks at 0.39 and 0.90 V vs. Ag/Ag^+ . The oxidation potentials of **2a** are higher and broader than those of **3**, indicating the apparent electronic interaction between the repeating thioketene dimer units in the π -conjugated system. Such anodic shifts and broadenings of the peaks have been observed in other electrochemically active π -conjugated polymers. The cast film of **2b** also gave similar broad oxidation peaks ($E_{\text{pa}} = 0.43$ and 0.92 V vs. Ag/Ag^+) to those of **2a** (Figure 3B). An apparent broad oxidation peak for **2** compared with that of **3** suggested the interaction between thioketene

dimer units along the π -conjugated polymer main chain.

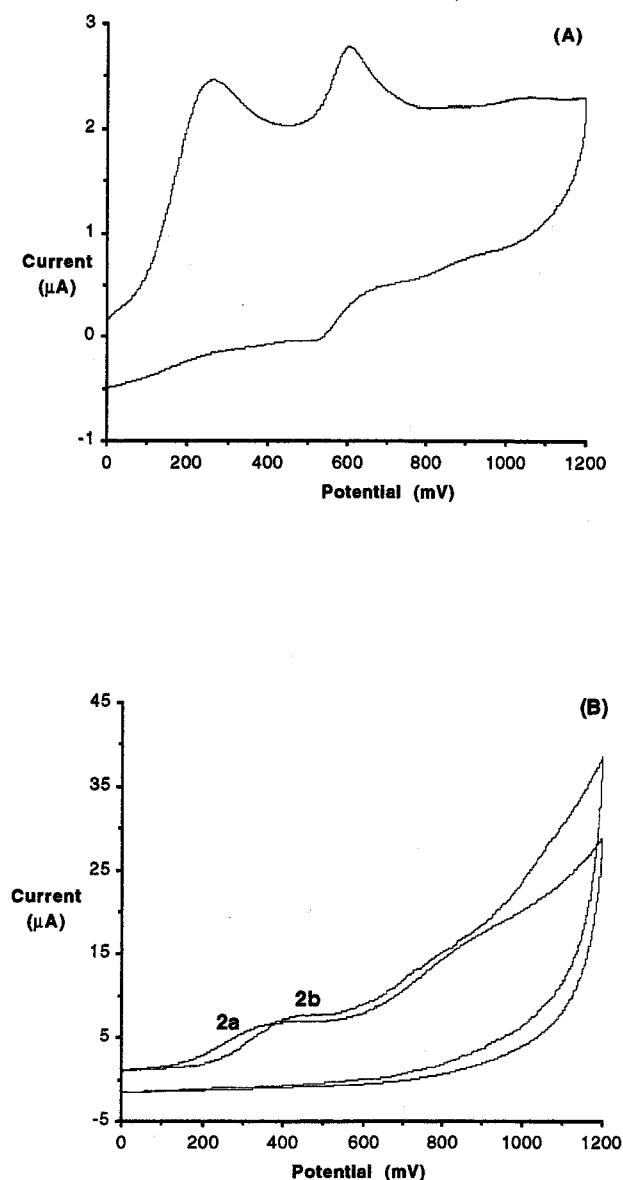
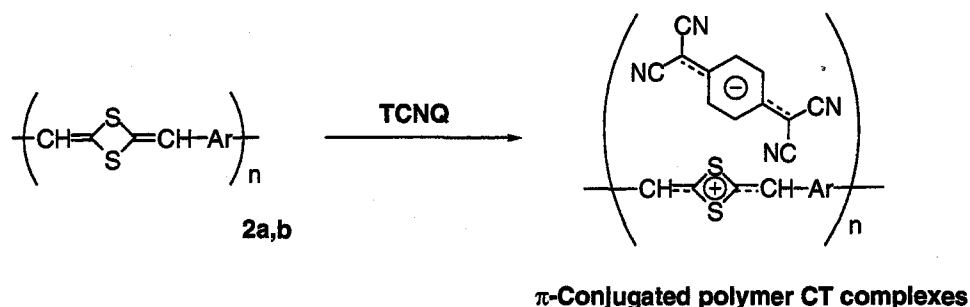


Figure 3. Cyclic Voltammograms of **3** (A), films of **2a** and **2b** (B) in CH_3CN solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 100mV/s.

Interestingly, DMSO solution of the model compound **3** turned to a clear green homogeneous solution after adding an excess amount of 7,7,8,8-tetracyanoquinodimethane (TCNQ) against **3**, indicating the formation of charge-transfer (CT) complex. Then the precipitated TCNQ, which was not reacted with **3**, was filtered off, and the filtrate was evaporated to give a green powder. This CT complex contained a 1:1 ratio of **3** to TCNQ, determined by elemental analysis. The polymers **2a** and **b** also formed green CT complexes

with TCNQ in DMSO (Scheme 2), prepared in the same manner as **3**. The ^1H NMR spectra of the polymer CT complexes in $\text{DMSO}-d_6$ as well as the elemental analyses also showed the formation of the complex containing 1:1 ratio of the repeating unit in **2** to TCNQ.

Scheme 2



The UV-vis absorption spectrum of the anion radical of TCNQ exhibits absorption maxima at 420 nm and between 600 and 900 nm.¹⁹ The neutral TCNQ shows a strong absorption at 392 nm. The UV-vis absorptions of the CT complexes of **2** and **3** with TCNQ in CH_3CN contained the total band assignable to the anion-radical and the neutral TCNQ. The spectrum of the CT complex of **2a** is largely different from that of **2b** (Figure 4). Comparison of both spectra suggested that **2a** preferred the formation of anion radical TCNQ in the CT state, on the contrary, the CT complex of **2b** was mainly composed of the neutral TCNQ. The CT states of the complexes may be explained by the oxidation potentials of **2** determined by CV analysis. Predominant formation of TCNQ anion radical in **2a** complex is caused by the strong electron donating ability of **2a**.

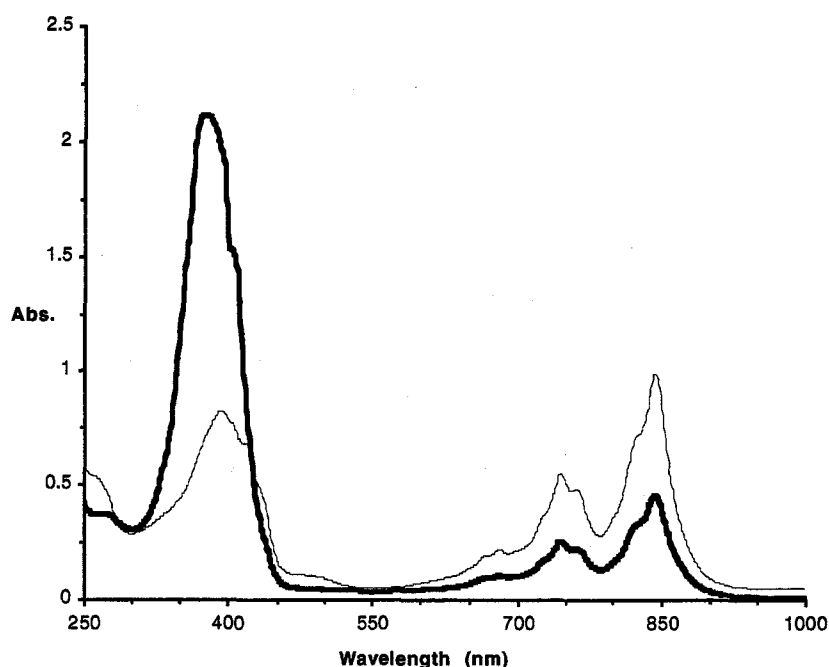


Figure 4. UV-vis absorption spectra of **2a**-TCNQ complex (plain line) and **2b**-TCNQ complex (bold line) in CH_3CN .

The CT complexes of **2** and **3** were measured by FT-IR to investigate the degree of CT in the solid state. The degree of CT can be determined by the frequency of the nitrile stretching band of TCNQ in the complex.²⁰ The spectrum of the CT complexes of the model compound **3** showed a C≡N band at 2178 cm⁻¹. This value indicates a fully ionic state (anion radical) of TCNQ in the sample. As same as the model compounds, the IR spectrum of the complex of **2a** with TCNQ showed one C≡N band at 2178 cm⁻¹, which is characteristic of TCNQ anion radical. The polymer CT complex of **2b** with TCNQ had a major band at 2178 cm⁻¹ and a minor band at 2202 cm⁻¹, showing that the complex contains two different species of charge transferred TCNQ. The former peak is corresponding to the anion radical of TCNQ, and the latter was due to a partially charge transferred TCNQ (degree of CT = 0.59).²⁰ As is similar to UV analysis, only the complex of **2b** contains the partially charge-transferred TCNQ in the solid state due to the weak electron donating property. However, the degree of CT between 0.5 and 1.0 is necessary for such complexes to achieve a high conductivity.

The conductivity of the polymer was investigated at room temperature by conventional two-probe technique. The polymer-TCNQ complexes of **2a** and **2b** showed the electrical conductivities of 9.5×10^{-5} and 2.0×10^{-4} S/cm, respectively, at room temperature. Higher conductivity of **2b** than that of **2a** might result from the existence of the partially charge transferred TCNQ. The polymer **2a** doped with iodine showed the conductivity of 1.8×10^{-3} S/cm.

Summary

In conclusion, the author prepared the polymers with thioketene dimer unit in the π -conjugated main chain by cycloaddition polymerization of aldothioketene. The UV-vis study indicated effective expansions of the π -conjugation system in the polymers. The polymers generally behaved as strong electron donors and formed CT complexes with TCNQ. Oxidation potentials and the CT states of the polymers were dependent on the aromatic moieties of the polymers. The TCNQ complex of **2b**, which contained the partially charge transferred TCNQ, had higher conductivity than that of **2a**. Possible applications of the new CT complexes composed of the thioketene dimers, including the low molecular weigh model compound, to electronic, magnetic and conducting materials are interesting, instead of the dithiafulvene-based compounds.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. The solvents were dried and distilled under N₂. Biphenyl-4,4'-bis(methyltriphenylphosphonium chloride) (**1b**) was synthesized according to the literature.²¹

Measurements. ¹H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. GPC measurement was carried out on TSK gel α -3000 by using DMF as an eluent at 40 °C after calibration with standard polystyrene samples. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer in CH₃CN solution of 0.1 M [NEt₄]BF₄ as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurements. For the CV of the polymers, thin polymer films were prepared on indium-tin-oxide (ITO) coated glass electrodes by casting from their solutions. The electrodes were dried under vacuum. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 source meter.

The polymer films were prepared by dropping of the polymer solutions onto glass plates equipped with platinum electrodes, followed by drying *in vacuo*.

Polymerization. To a mixture of a bis(triphenylphosphonium chloride) (1.0 mmol) and Et₂O (10 ml), a solution of phenyllithium in cyclohexane-Et₂O (ca. 17 %, 1.1 ml) was added dropwise at room temperature. After 0.5 h, carbon disulfide (152 mg, 2.0 mmol) was added to the mixture. After 5 h, the resulting yellow mixture was poured into a large quantity of MeOH (200 ml), and then left at room temperature for 12 h to effect the polymerization. The precipitate was collected and washed with Et₂O several times to remove impurities. After drying under reduced pressure, a brown polymer was obtained.

2a. Yield: 138 mg (54 %). ¹H NMR (270 MHz, DMSO-*d*₆) δ 5.1 (-CH₂PPh₃Cl), 6.7 (terminal benzene), 7.1-7.5 (repeating benzyldene proton), 7.6-7.8 (repeating benzene and triphenylphosphine), 7.9 (triphenylphosphine). IR (NaCl) 1653 cm⁻¹.

2b. Yield: 113 mg (30 %). ¹H NMR (270 MHz, DMSO-*d*₆) δ 5.1 (-CH₂PPh₃Cl), 6.9-7.2 (repeating benzyldene proton), 7.2-7.9 (repeating benzene and triphenylphosphine). IR (NaCl) 1655 cm⁻¹.

2,4-Dibenzylidene-1,3-dithietane (3). The model compounds **3** were prepared according to ref. 10c. ¹H NMR (270 MHz, (DMSO-*d*₆) δ 6.98 (m, 2H), 7.14 (m, 2H), 7.3-7.5 (m, 4H), 7.5-7.7 (m, 4H); IR (NaCl) 1652 cm⁻¹.

CT Complexes of 2 with TCNQ. An excess amount of TCNQ against repeating unit of **2** was added to the solution of **2** in DMSO, and the mixture was stirred for 15 min. The solution gradually became dark green. After the unreacted TCNQ was filtered off, the solvent was evaporated to obtain a dark green powder.

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Chapter 11

Electron Accepting Si-Si Bond in Linear Framework by Combination with Thioketene Dimer Unit

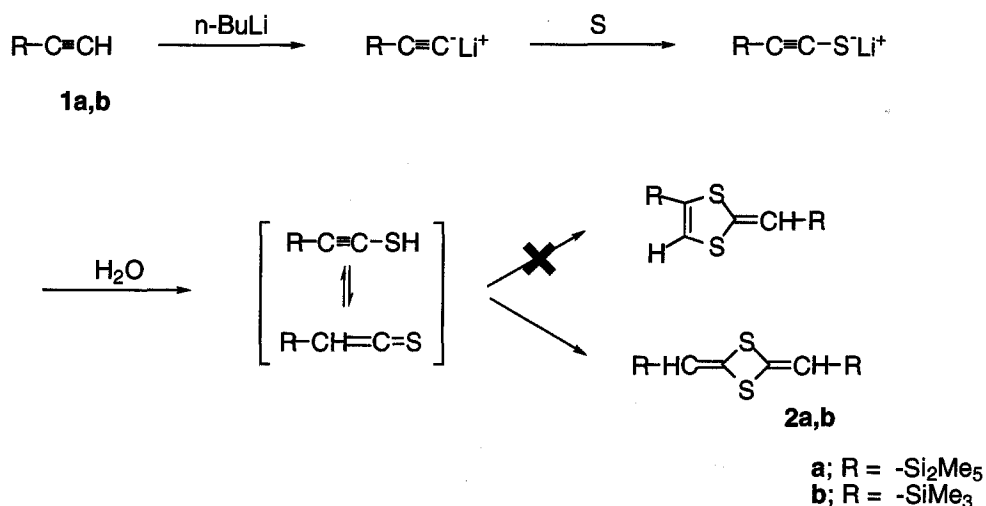
Abstract: A series of silyl and disilyl substituted thioketene dimers (2,4-diylidene-1,3-dithietane), including polymers, have been synthesized. Calculation of the HOMO and the LUMO of 2-disilylidene-4-ylidene-1,3-dithietane by PM3 semi-empirical molecular orbital method suggested an effective charge transfer (CT) from the thioketene dimer to the Si-Si bond. This prediction was confirmed by UV-vis spectrum of 2,4-bis(pentamethyldisilylidene)-1,3-dithietane, which showed the intramolecular CT absorption in visible range. The CT interaction of a polymer with the thioketene dimer and the Si-Si units was enhanced more efficiently due to an elongation of the σ - π conjugation. The absorption in the spectrum of the polymer showed a negative solvatochromic behavior, which is characteristic of the intramolecular CT interaction. Sun light exposure decreased the intensity of the CT absorption, suggesting that inefficient σ - π conjugation resulted from transformation and degradation of the Si-Si unit led to decrease the CT.

Introduction

Organosilicon compounds have been widely utilized not only as various functional materials but also as valuable organic synthetic reagents owing to their unique chemical and physical properties.¹ There has been a remarkable growth in electro- and photo-chemistry of organosilicon compounds over the past two decades. Electronic state of cyclic and acyclic silicon catenates differs significantly from those of their carbon analogue. Low ionization potential (I_p) of a Si-Si bond leads to similar properties to a carbon-carbon double bond (electronic delocalization within the σ -bonded framework) and effective electron donating property.² Electron delocalization between the Si-Si σ bonds and π systems has been also conclusively established in various disilyl compounds containing unsaturated or aromatic groups,³ which are important as semiconductors or conductors⁴, and light emitting materials⁵. In this chapter, the author reports the synthesis of disilyl substituted thioketene dimers and demonstrates that effective σ - π conjugations induce the unique charge transfer (CT) from the thioketene dimer to the Si-Si units, even though the Si-Si unit usually acts as an electron donor.

Results and Discussion

Scheme 1



Scheme 1 shows the preparation of the thioketene dimers having silyl and disilyl moieties (**2**). Reaction of ethynyl compounds (**1**)^{3d} with n-BuLi and sulfur yielded alkynyl thiolates *in situ*. Treatment with water generated unstable silylthioketenes, which rapidly dimerized to form **2** in excellent yields. The structures of the obtained dimer compounds **2** were supported by IR, ¹H, ¹³C NMR spectra and elemental analysis. The author first expected that the corresponding dithiole compounds should be obtained, since the usual results of this reaction, in the case of aromatic thioketenes, yield dithioles by [2+3] cycloaddition reaction between aldothioketenes and their alkynethiol tautomers.⁶ However, all spectral data of **2** indicated the [2+2] cycloaddition of aldothioketenes to give 2,4-diylidene-1,3-dithietane structures.⁷

Calculation of HOMO and LUMO of disilyl substituted thioketene dimer (**2c**) using the PM3 Hamiltonian was carried out. The thioketene dimer and the Si-Si moieties bear the most of the electron density of the HOMO, while atomic coefficients

of the LUMO are larger on the Si-Si fragment (Figure 1). In Chapter 10, the author described that such thioketene dimer unit shows very strong electron donating property.^{7d} These results predicted that direct attachment of a strong donor such as the thioketene dimer to the Si-Si bond would lead to intramolecular CT from the donor to the Si-Si moiety. Interestingly, the Si-Si unit has been regarded as an electron donor so far. The PM3 calculation of a thioketene dimer having one trimethylsilyl moiety showed no observation of the electron density of the LUMO on the silicon atom, suggesting less available for CT. The CINDO/S calculation for the electron transition spectrum of **2a** suggested that a peak due to the HOMO-LUMO transition would appear at 429 nm.

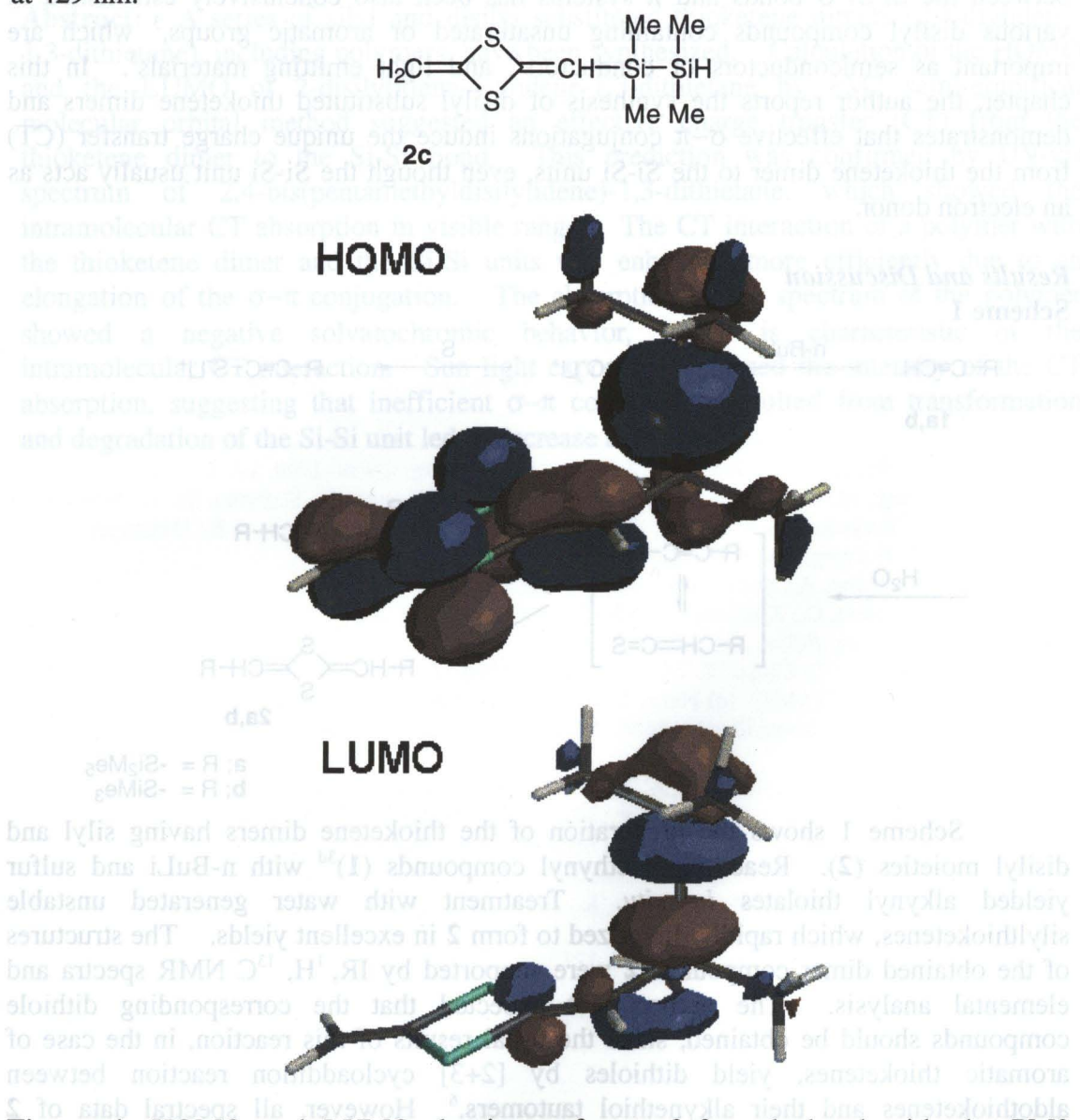


Figure 1. HOMO and LUMO density surfaces of **2c** calculated with the PM3 Hamiltonian. The density value is 0.002 electrons/au³.

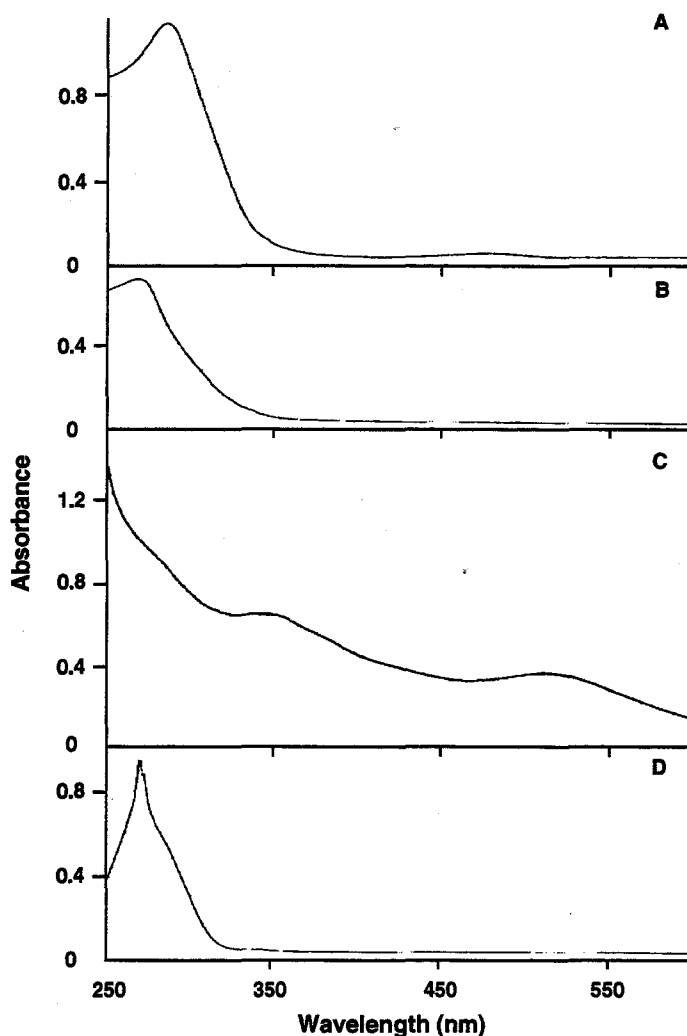


Figure 2. UV-vis spectra of thioketene dimers; (A) **2a** and (B) **2b** in CHCl_3 , (C) **4a** and (D) **4b** in CH_3CN .

In the UV-vis spectrum, the bis(silyl)-substituted thioketene dimer (**2b**) shows a peak due to the $\pi\text{-}\pi^*$ transition at 268 nm. The absorption maximum (282 nm) of the bis(disilyl)-substituted thioketene dimer (**2a**) moved to the direction of lower energy, indicating the presence of $\sigma\text{-}\pi$ conjugation. The spectrum of **2a** shows small but important absorption ($\epsilon = 530$) with a peak at 463 nm, however, **2b** shows no absorption in this region in CHCl_3 (Figure 2A and B). Since the peak intensity of the absorption in **2a** was proportional to the concentration of the sample solution, the absorption in the visible region of **2a** should be originated from the intramolecular CT interaction between the Si-Si and the thioketene dimer unit. The CT absorptions of **2a** showed interesting behavior in various solvents. The peak moved to shorter wavelength, with increasing the solvent polarity (Figure 3; $\lambda_{\text{max}} = 446$ nm in CH_3CN and 455 nm in acetone). This solvent-dependent shift is characteristic of negative-solvatochromism, which is clearly caused by the intramolecular CT interaction.⁸ If, with increasing solvent polarity, the ground-state molecule is better stabilized by solvation than molecule in the excited state, negative solvatochromism would result.⁹

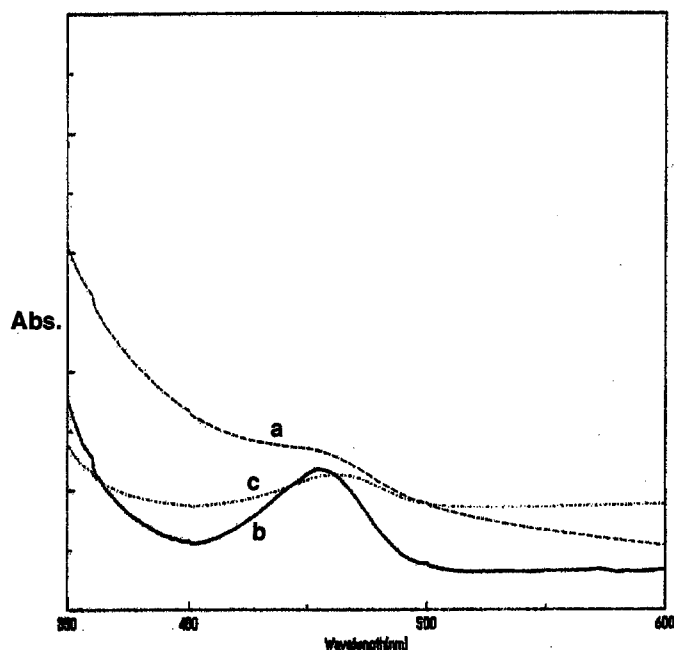
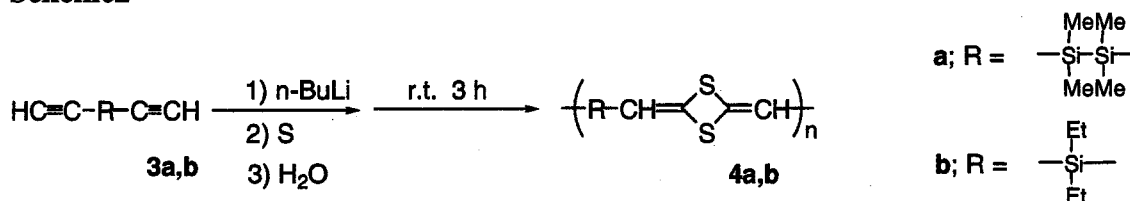


Figure 3. CT absorption of **2a** in CH_3CN (a), in acetone (b) and in CHCl_3 (c).

Scheme 2



The author also carried out the polymerization by use of a disilanylene monomer **3a**^{3d} aiming at preparation of a novel σ - π conjugated polymer **4a** (39 % yield, $M_n = 7890$, Scheme 2). The IR and NMR spectra of **4a** were similarly to those of CT complexes of **2** with strong acceptors. The thioketene dimer compounds **2** interact with strong acceptors such as iodine and tetracyanoquinodimethane (TCNQ) by CT effect. The peaks for C=C vibration of the thioketene dimer unit of **2a** and **2b** shifted to 1616 and 1627 cm^{-1} , respectively, after treatment with iodine. The IR spectrum of **4a** showed the corresponding peak at 1625 cm^{-1} . After **2a** and **2b** were mixed with iodine or TCNQ, the peaks in the ^1H and ^{13}C NMR spectra corresponding to the thioketene dimer moiety were hardly recognized. The ^1H and ^{13}C NMR spectra of only **4a** showed broad signals for the thioketene dimer moiety. These results indicate the effective CT interaction between the thioketene dimer and Si-Si bond in **4a**. The paramagnetic species in **4a**, which is also observed in ESR spectrum, should cause the broad resonance peaks of **4a** in NMR.

This polymer **4a**, unlike the low molecular weight compounds **2**, shows a very large absorption ($\epsilon = 3310$) with a peak at 515 nm in CH_3CN (Figure 2C), which was located at longer wavelength compared with that of **2a**. This fact indicates that extensive σ - π delocalization enhanced the CT interaction between the units. The strong and broad absorption across the entire spectral region of **4a** is owing to the effective σ - π conjugation, which overlaps with the CT transition in the visible range.

The extinction of the CT band varied in accordance with Lambert-Beer law, also indicating the intramolecular CT in **4a**. Similarly to **2a**, a clear negative-solvatochromism of the CT band of **4a** was observed (Figure 4; λ_{max} = 488 nm in H₂O, 495 nm in MeOH, and 519 nm in acetone). Sun light exposure decreased the intensity of the CT absorption of **4a** (Figure 5), suggesting that transformation of the Si-Si unit to a siloxane (Si-O-Si) and/or degradation of the polymer chain led to an inefficient CT interaction.¹¹ This short-time decrease of the absorption indicates the very low stability of **4a** against the light. A peak for Si-O-Si unit around 1100 cm⁻¹ also became appeared in IR spectrum of **4a** after sun light exposure.

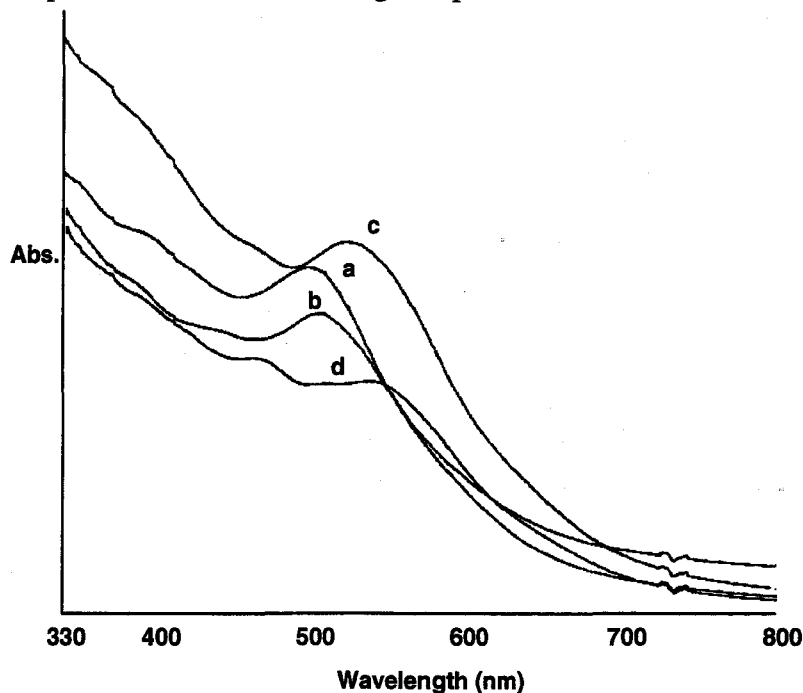


Figure 4. CT absorption of **4a** in H₂O (a), in MeOH (b), in CH₃CN (c), and in acetone (d).

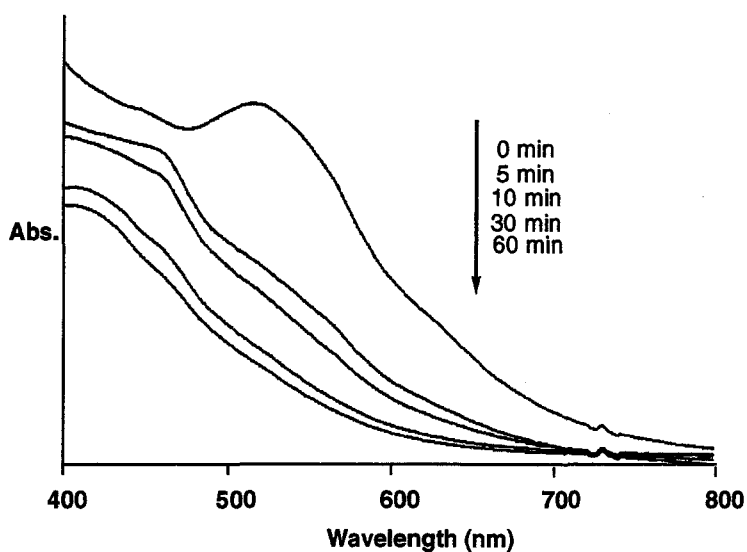


Figure 5. Time dependence of CT absorption of **4a** by sun light exposure.

The author also prepared a non-conjugated polymer **4b** by cycloaddition polymerization of bithioketene derived from diethynylsilane **3b** (Scheme 2). In contrast to **4a**, the obtained polymer **4b** (24 % yield, $M_n = 7100$) had no absorption in the visible range (Figure 2D) in the UV-vis spectrum, suggesting no CT interaction between the thioketene dimer and the Si unit in the polymer. The fact that the absorption maximum of **4b** was same as that of **2b**, suggests that π -electrons on the thioketene dimer are hardly delocalized through the polymer chain.

Summary

A series of silyl substituted thioketene dimers have been synthesized. The interesting fact of the CT from the thioketene dimer unit to the Si-Si bond was demonstrated. No intramolecular CT transition was observed in the systems of the thioketene dimers attached to the silyl or the silylene unit. To achieve the effective intramolecular CT interaction between the units, eventually, the σ - π conjugation system would be required.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2 .

Measurements. 1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. IR spectrum was recorded on a Perkin Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography was carried out on TSK gel α -3000 by using DMF as an eluent at 40°C after calibration with standard polystyrene samples. ESR spectra were recorded at X-band frequency with JEOL JES-RE spectrometer in quartz capillaries of 4 mm internal diameter. HOMO and LUMO density surfaces of **2c** was calculated by use of the Spartan Package; Wavefunction, Inc., Irvin, CA, USA. The molecular orbital surfaces were created after calculation of geometry optimization by PM3 semi-empirical molecular orbital method. The electron transition spectrum of **2a** was calculated by the CINDO/S method implanted in the MOS-F ver 4.2; Fujitsu Ltd., Tokyo, Japan, after the molecular structure of **2a** was optimized by PM3 semi-empirical method.

1-Ethynyl-1,1,2,2,2-pentamethyldisilane (1a).^{3d} Under N_2 atmosphere, 1-chloro-1,1,2,2,2-pentamethyldisilane (2.66 g) in THF (3 ml) was added to 0.5 M ethynylmagnesium bromide in THF solution (40 ml) over 15 min at room temperature. After completion of the addition, the mixture was heated to reflux for 5 h. After cooling, n-hexane (5 ml) and 1N aqueous HCl (5 ml) was added. The organic layer was separated and washed twelve times with 1N HCl (5 ml). The combined aqueous layer was extracted with n-hexane (5 ml) three times. The combined organic layer was washed with 1N HCl (5 ml) six times. The hexane solution was dried with $MgSO_4$ and evaporated. The residual yellow liquid was distilled to give colorless product (1.91 g, 77 % yield).

1,2-Diethynyl-1,1,2,2-tetramethyldisilane (3a).^{3d} Compound **3a** was obtained from 1,2-dichloro-2,2-dimethyldisilane in a similar manner (82 % yield).

Diethynyldiethylsilane (3b).^{3d} Compound **3b** was obtained from dichlorodiethylsilane in a similar manner (98 % yield).

Preparation of 2. To a solution of ethynyl compound **1** (1 mmol) in Et₂O (1 ml), 1.6 M solution of *n*-butyllithium in hexane (0.63 ml) was added at 0°C. After stirring for 0.5 h, the powder of sulfur (32 mg) was added to the solution. The reaction mixture was stirred for 2 h, then cooled at -78°C and water (1 ml) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 0.5 h. The mixture was extracted with Et₂O and the combined organic solution was dried over Na₂SO₄. After evaporation, the residue was purified by chromatography on silica.

2,4-Bis(pentamethyldisilylidene)-1,3-dithietane (2a). Compound **2a** was obtained from 1-ethynyl-1,1,2,2,2-pentamethyldisilane (**1a**) after purification by chromatography on silica using hexane/ethyl acetate (50/1) as an eluent (92 %). Mp 145-49 °C; IR (NaCl) 1532 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.09 (m, 18H), 0.19 (m, 12H), 6.62 (s, 2H); Anal. Calcd: C, 44.62; H, 8.56. Found: C, 44.29; H, 8.60.

2,4-Bis(trimethylsilylidene)-1,3-dithietane (2b). Compound **2b** was obtained from trimethylsilylacetylene (**1b**) after purification by chromatography on silica using hexane/ethyl acetate (20/1) as an eluent (85 %). Mp 79-80 °C; IR (NaCl) 1534 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.19 (s, 18H), 6.58 (s, 2H); ¹³C NMR (270 MHz, CDCl₃) δ 0.22, 141.43, 142.19; Anal. Calcd: C, 46.09; H, 7.73. Found: C, 45.54; H, 7.74.

Polymerization. To a solution of diethynyl monomer **3** (1 mmol) in Et₂O (1 ml), 1.6 M solution of *n*-butyllithium in hexane (1.25 ml) was added at 0°C. After stirring for 0.5 h, the powder of sulfur (64 mg) was added to the solution. The reaction mixture was stirred for 2 h, then cooled at -78°C and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. The mixture was then poured into a large quantity of Et₂O. The obtained precipitate was extracted with acetone repeatedly. After evaporation of the combined acetone solution, polymer **4** was obtained.

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List of Publications

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Chapter 1

Synthesis of π -Conjugated Poly(dithiafulvene) by Cycloaddition Polymerization of Aldothioketene with Its Alkynethiol Tautomer

Naka, K.; Uemura, T.; Chujo, Y.

Macromolecules **1998**, *31*, 7570-7571.

Synthesis of π -Conjugated Poly(dithiafulvene) by Cycloaddition Polymerization of Aldothioketene with Its Alkynethiol Tautomer. Polymerization, Optical Properties, and Electrochemical Analysis

Naka, K.; Uemura, T.; Chujo, Y.

Macromolecules **1999**, *32*, 4641-4646.

Chapter 2

Linearly Extended π -Conjugated Dithiafulvene Polymer Formed Soluble Charge-Transfer Complex with 7,7,8,8-Tetracyanoquinodimethane

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Chapter 3

Synthesis and Properties of π -Conjugated Poly(dithiafulvene)s by Cycloaddition Polymerization of Heteroaromatic Bisthioketenes

Naka, K.; Uemura, T.; Chujo, Y.

Macromolecules **2000**, *33*, 4733-4737.

Chapter 4

π -Conjugated Poly(dithiafulvene)s and Poly(diselenafulvene)s: Effects of Side Alkyl Chains on Optical, Electrochemical and Conducting Properties

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Submitted to *Macromolecules*.

Chapter 5

Synthesis and Properties of Oxygen, Methylene and Alkylene Bridged Poly(dithiafulvene)s

Marathe, S.; Uemura, T.; Naka, K.; Chujo, Y.

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Chapter 6

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Chapter 8

Self-Complexation of Poly-Conjugated Donor Molecule with Cyclic Acceptor

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Chapter 9

Conjugative Effect through Saturated Ethylene Chain; Enhancement of $\sigma^*-\pi^*$ Conjugation by Intramolecular Charge-Transfer

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Chapter 10

Synthesis of a π -Conjugated Poly(thioketene dimer) and Its Electron-Donating Property

Uemura, T.; Naka, K.; Gelover-Santiago, A.; Chujo, Y.

Macromolecules **2001**, *34*, 346-348.

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